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THE CHEMISTRY OF FIRE AND FIRE PREVENTION

A HANDBOOK FOR INSURANCE SURVEYORS, WORKS' MANAGERS, AND ALL INTERESTED IN FIRE RISKS AND THEIR DIMINUTION

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PREFACE.

THE present work is based upon two courses of lectures delivered by one of the authors to an audience composed of gentlemen connected with the Fire Insurance Profession.

The need for a text-book dealing mainly with the Chemistry of Fire Insurance matters has frequently been brought before the notice of the authors by requests from various quarters to recommend such a work.

In response to the evident demand for such a book, the lectures, considerably extended and rearranged, are now published in this volume.

A difficulty has been felt in the preparation of the book, to keep to the middle course, between an elementary science manual (to which some parts of the book certainly show a resemblance) and a technological account of manufacturing processes requiring a considerable knowledge of chemistry on the part of the reader. The authors are conscious that they have sometimes failed to properly keep to this desired track and that the book lacks "balance."

The subjects dealt with are numerous and diverse, the description of the various industrial operations necessarily brief and imperfect, but in all cases an attempt has been made to show, as clearly as possible, the principles upon which the processes are based and in what the special risks of fire consist.

Manufacturers will understand that many processes which appear dangerous to an outsider are safe in practice, because the conditions under which they are worked render the risks of fire virtually non-existent.

Still, in such cases, the old adage "familiarity breeds contempt" is true, and a slight deviation from the usual course of treatment may render the process highly dangerous. The authors have therefore endeavoured to point out under what conditions these dangers may arise, and trust that the book may prove useful to the manufacturers themselves.

A short explanatory chapter on the meaning and use of chemical terms and formulæ has been incorporated for the use of those readers who possess but little knowledge of science and scientific phraseology.

To many friends in Leeds and district, connected with

Fire Insurance, the authors desire to express their indebtedness for the loan of books and pamphlets relating to Insurance matters. They would also take this opportunity of thanking Mr. H. R. Procter, Professor of Leather Industries in the Yorkshire College, for valuable help, particularly with reference to the subjects dealt with in Chapters IX. and X.

In conclusion, the authors would welcome any suggestions or criticisms for use in a possible future edition.

THE YORKSHIRE COLLEGE, LEEDS, and
KIRKCALDY, N. B.

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CHAPTER I.

INTRODUCTORY.

Early Views as to Fire—Air Always Concerned in the Processes of Combustion—Physical and Chemical Nature of the Atmosphere—Properties of Its Chief Constituents—Some Phenomena Connected with Combustion.

When and how man made his first acquaintance with fire is a question which history and science are alike unable to answer. The means of procuring it were always at hand, but their discovery was probably made in an age long after man had learnt its use. The lightning, subterranean fires and spontaneous combustion of various natural products were, most likely, the sources from which our ancestors first learnt to apply it as a source of heat in cold weather. A fire, once ignited, was tended with care, and a tribe, when travelling through a country, carried with them a piece of burning or smouldering bark, which they blew into a flame to kindle a fire at their various halting places, just as some Australian races do to this day. At last, some one, more ingenious than his fellows, hit upon a plan of procuring it at will, either by rubbing two sticks together, or, perhaps, by means of two hard stones. A very great advance, for man then had in his hands the means of obtaining, whenever he wished, a most powerful agent. Probably the discovery of a method of artificially producing fire ranks as one of the most important events in the history of humanity. Primeval man, recognising its power, was not slow to ascribe to it a divine source, hence arose the Fire-worshippers, who still survive among Eastern nations.

The awe and respect paid to fire naturally attracted the attention of thinkers and philosophers, and it is not surprising, therefore, that it played an important rôle in ancient schools of thought. To Aristotle, fire was one of the four "elements" (earth, air, fire and water) of which all substances were supposed to be composed; a view held by many of the alchemists of the middle ages, the term "element," however, being used in a different sense to its modern one and signifying rather a quality or property than a substance. Thus "fire" meant the qualities of "hotness and dryness," and substances endowed with these attributes were said to contain "fire."

Another view held by the chemists of the eighteenth century attributed the property of combustibility to a principle which they called "phlogiston." According to this theory, substances which readily burn do so because of their richness in phlogiston; burning, in fact, consists in the loss of that principle, and the products left are the original substance less the phlogiston escaped.

This doctrine was almost universally held until the great French chemist, Lavoisier, at the end of the last century, effected its overthrow. He pointed out more clearly than had been done before, that the residue left after burning a metal weighed more than the original substance. Hence, instead of a substance losing phlogiston in the act of burning, it gained something from the air, and combustion consisted in chemical union of the combustible substance with a constituent of the air, this act of combination being attended by the liberation of light and heat. It is to these views of Lavoisier that we owe our modern conceptions of the nature of combustion. It will be shown later that every substance before it will combine with a portion of the air, *i.e.*, before it will burn, must have its temperature raised up to or above a certain point. We may obtain heat enough to reach this temperature, and so set fire to the body either by—

(1) *Mechanical Means.*

(a) By resistance to motion in the friction of substances moving against each other, this method, as already mentioned, was, and still is, used by some savage races in order to obtain fire; pieces of dry wood are vigorously rubbed together, until they produce heat sufficient to ignite them. A more common application of the same method was furnished by the flint and steel of our forefathers.

(b) Heat is also developed by the sudden compression of a substance, *e. g.*, a gas.

(2) *Chemical Action.*—This may be the union of another substance with air, as in most cases of starting a fire, when we use a match or taper, etc.; or it may be the slow combustion occurring when the substance itself is merely exposed to air. Phosphorus, for example, thus ignites itself in time; at first, combination between phosphorus and the air takes place without flame, and heat is gradually produced, and increases until the igniting temperature of phosphorus is reached and the mass takes fire.

(3) *The Sun's Rays.*—These may be focussed by means of a lens or mirror and produce a very high temperature (occasionally by the "bull's-eyes" still found in some old windows in mills, etc.).

(4) *Electrical Resistance.*—*Whenever a current of electricity flows through a conductor heat is produced,*

this heat is greater, the greater the quantity of electricity or the less the conductivity of the conductor. The electric spark, lightning and the arc are merely exaggerated cases of such heat production. (See p. 110.)

(5) *The Earth's Internal Heat.*—This is exhibited in the higher temperature found in descending a mine, and, perhaps, by the intensely high temperature of the matter ejected from volcanoes, etc.

Since in the actual combustions that occur in nature or in daily life the chemical action involved is, nearly always, the union of the combustible with one of the constituents of the air, it is evident, at the very outset, that a knowledge of the nature and properties of the atmosphere is of the greatest importance.

Air is a material substance and, as such, possesses weight, that is, it is pulled vertically downwards, or is attracted, by the gravitation of the earth. This fact, though now well known, escaped the notice of the early philosophers, since in their experiments it was found that a bladder weighed the same whether it were full of air or empty and flaccid. But, thanks to the exertions of later philosophers, by using a rigid vessel, *e.g.*, a hollow sphere of glass, and weighing it when full of air, then extracting the air from it by means of an air-pump and weighing again, it can easily be shown that air has weight.

This experiment, conducted with great care, shows that 1000 cubic feet of air weigh (when the temperature is 32° F. and the barometric pressure is 30 inches of mercury) about 80½ pounds or, more accurately, 1 litre of air at 0° C. and 760 mm. pressure weighs 1.293 grammes. In consequence of this weight, the air is pulled down to the surface of the earth, and so the portions beneath are pressed upon and compressed by the weight of those above; therefore, all bodies on or near the surface of the earth are subjected to the pressure of the air which surrounds them. The magnitude of this pressure is very considerable, amounting on the average to about 14¾ pounds per square inch. It is exerted upon everything and everybody, a man of average size being pressed upon by a total force equal to the weight of about 14 tons. This is not ordinarily perceptible, since it is exerted equally in all directions, but becomes apparent when the pressure is removed from any portion of the body, as, for example, by the use of cupping glasses, etc. The material nature of air is also rendered evident by the resistance which it offers to the rapid motion of bodies immersed in it or the action exerted upon stationary objects when the air is in motion (wind).

The pressure of the air is measured by an instrument known as the *barometer*. This was invented by an Italian physicist, Torricelli, in 1643 (Fig. 1). In its simplest form it consists of a glass tube 32 or 34 inches long, closed at one end and open at the other. The tube is completely filled with mercury and inverted (the open end being temporarily closed by the thumb) into a trough of mercury; the thumb is then removed, the end of the tube being below the surface; the mercury falls in the tube a few inches, and remains so that its surface is about 30 inches above that in the trough. It tends to sink, owing to gravitation, but is prevented by the pressure of the atmosphere acting upon the surface of the mercury in the trough; equilibrium is reached when the pressure exerted by the column of mercury is equal to the pressure of the air.

This simple form of barometer is the best and, with adequate means of measuring the vertical height between the surfaces of the mercury inside the tube and in the trough, is the one always used when the correct barometric pressure of the air is required.

The ordinary *weather-glass* or *siphon barometer* (Fig. 2), depends upon the same principle, but by means of a somewhat unsatisfactory device the alterations of level of the mercury surface are multiplied so as to be more easily visible on the dial. This form of instrument, though fairly sensitive, has no claims to accuracy, that is, though it will indicate the fact that a very slight change in barometric pressure has occurred, it will not accurately measure either that change or the real height of the barometer.

Fig. 1—Torricellian Barometer.

Fig. 2.—Siphon, or Wheel, Barometer.

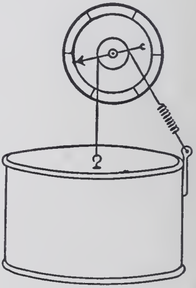

Fig. 3.—Aneroid Barometer.

Another form possessing great advantage in portability, the *aneroid barometer,* depends upon quite a different principle. In it the essential part is a box, usually of a flat cylindrical form, made of thin steel, completely evacuated and hermetically sealed. (Fig 3).

The pressure of the air on the outside causes the box to partially collapse; the top and bottom of the cylinder, being flat and thin, are most affected; the amount of this deformation will be greater when the pressure is greater, and less (for the elasticity of the steel will cause the box to more nearly reassume its original form) when the pressure decreases. The movements of the top or bottom, or both, are rendered more evident by a multiplying arrangement, as shown in the figure.

Since the height of the barometer depends upon the pressure, which, in turn, depends upon the weight of the air above any particular place, it is evident that the higher we ascend above the surface of the earth the less air we shall have above us, and that the pressure will, therefore, diminish. Hence the barometer can be used for measuring altitudes. (It is found that by ascending about 900 feet the barometer falls about 1 inch.)

Air, in common with all other gases, is greatly influenced by changes in temperature and pressure. If the former remain constant, the volume of a given quantity of air varies inversely as the pressure (Boyle's law). In other words, if the pressure on a certain quantity of air be doubled, it will be reduced to one-half its original volume, and conversely, if a quantity of air be caused to expand to double its original volume, it will exert only one-half its original pressure.

If the pressure be kept constant and the temperature vary, the volume will alter in accordance with the following law: the volume is directly proportional to the temperature, expressed in degrees, measured from the *absolute zero* of temperature, *i.e.*, from a point 273° C. or 491° F. below the melting point of ice (= —273° C. or —459° F.).

For example, suppose 100 cub. ft. of air at 15° C. be warmed to 20° C. and the pressure be kept constant, the volume will now be $100 \times \frac{293}{288} = 101.74$ cub. ft. These laws with reference to the influence of changes of pressure and temperature apply to all gases alike.

CHEMISTRY OF THE ATMOSPHERE.

When combustible substances are burnt in a confined volume of air the latter, after a time, becomes quite unfitted to support the combustion of any further quantity of combustible. A similar exhaustion of the air is observed in the respiration of animals.

Much information can be obtained by carefully studying the action of various combustible substances upon a confined volume of air.

A candle placed in a closed jar of air soon goes out, and if a fresh candle be introduced it is at once extinguished, whereas a piece of burning phosphorus will continue to burn therein for some time. After the combustion of the phosphorus has ceased, the air will be found to be quite unable to support further combustion of any ordinary substance.

When phosphorus is burnt in air dense white clouds are produced, slowly settling down as a white crust, and easily absorbed by water. If the experiment be performed in a bell jar standing over water, it will be found that after the phosphorus has ceased to burn the white fumes will slowly disappear, and eventually there will be obtained a residue of a perfectly colourless gas, which will not support combustion or respiration, constituting about four-fifths of the total volume of the air taken (Fig. 4).

Thus it is seen that only a comparatively small portion of the air takes part in the combustion of even such an inflammable substance as phosphorus.

The residue, first examined and described by Rutherford, consists mainly* of a gas which has received the name *nitrogen*, from the fact that it is a constituent of nitre or saltpetre.

The properties of this gas are not very interesting, since it is chiefly remarkable for its chemical inactivity.

As a general rule it plays practically no part in the processes of combustion or respiration which take place in air. Only in the case of some comparatively rare substances does any combination with nitrogen occur when

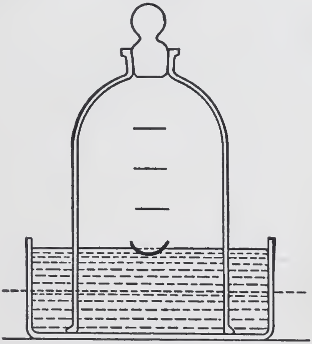

FIG. 4.—Apparatus for burning Phosphorus in a Confined Volume of Air.

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* In addition to oxygen and nitrogen, air contains carbon dioxide, aqueous vapour, argon, and traces of other substances. Aqueous vapour and carbon dioxide vary in amount; the latter being increased by combustion and the respiration of animals. In pure country or sea air the average amount is about .03%, its presence is of the greatest importance, since plants obtain from it the whole of the carbon of which so large a portion of their tissues is composed. The other constituent, argon, discovered in 1894–5 by Lord Rayleigh and Prof. Ramsay, is present to the extent of nearly 1%, and is left when the oxygen is removed by means of combustibles. In fact, the so-called nitrogen left when phosphorus is burnt in air contains 1.2% argon. Argon, like nitrogen, is chiefly remarkable for its negative properties. It is 19.9 times as heavy as hydrogen, and seems to be incapable of combining with other substances. It is therefore of no practical importance so far as we know at present. Other constituents have been discovered by Ramsay, but they are present only in traces, and are of no importance to us.

the air is brought in contact with hot bodies. It mainly acts, therefore, as a diluent of *oxygen,* the constituent concerned in the processes to which we have just referred, and removed (by being converted into compounds) when combustibles are burnt in air. Consequently this substance, oxygen, is of great importance, and it is certainly desirable that we should be familiar with its more important properties.

Oxygen was discovered rather more than a century ago by Joseph Priestley. He obtained it in August, 1774,

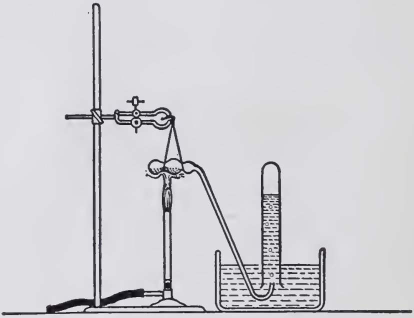

Fig. 5.—Preparation of Oxygen from Mercuric Oxide.

by the action of heat upon a substance known then as "red precipitate," formed by heating quicksilver with free exposure to air. The quicksilver under this treatment slowly becomes covered with a red scaly powder, now recognised as oxide of mercury.

When this red powder is heated it splits up into its constituents, mercury (quicksilver) and oxygen. The former, evolved first as a vapour, quickly condenses and forms tiny globules of liquid mercury; the latter, a gas, may be collected in a tube or jar filled with water and standing in the pneumatic trough (Fig. 5). This method, though historically interesting, is of little importance, as it is not at all suited for the preparation of considerable quantities of the gas. (See Chap. III.)

The most remarkable property of oxygen is its exceptional tendency to combine with other elements, which act of combination is generally attended by the production of light and heat. Any substance which will burn in air burns with increased vigour in oxygen; and some materials, not of themselves producing sufficient heat to sustain their combustion in air, and which, therefore, only oxidise rapidly under the influence of some external source of heat, will burn quite easily in pure oxygen, for here the cooling action exerted by the indifferent constituents of the air is absent.

To illustrate the great activity of oxygen in promoting combustion reference may be made to the brilliancy with which sulphur, phosphorus and a candle burn in it; in all cases a much brighter light and a higher temperature is produced than when the same substances burn in air. So, too, iron, which can only oxidise in dry air when its temperature is kept up by some external source of heat, is found to burn brilliantly, when once started, in pure oxygen (Figs. 6 and 7).

Although from the above instances it is seen that the temperature of substances burning in oxygen is much higher than when burning in air, *the total quantity of heat evolved by the oxidation of a given weight of any material is the same, whether it be burnt in air or oxygen, or whether it be burnt slowly or quickly.* This fact, perhaps surprising to those not before acquainted therewith, is of great importance and must be borne in mind.

There are several reasons for the higher temperature of flames burning in oxygen—

(1) The flame is smaller for the same quantity of material burnt, as the vapours and gases of the combustible have not to spread themselves over so great a space in order to find sufficient oxygen with which to combine; thus, the same quantity of heat is produced in a smaller space and the temperature is higher.

(2) The nitrogen and other inert gases present in air, carrying off a considerable amount of heat and thus reducing the temperature of the flame, are absent.

Combustion is so important a subject that we may now very suitably consider some of the circumstances under which it occurs. As already stated, almost all examples of combustion really consist in union with oxygen, the energy set free appearing as light and heat. Mere contact of a substance with oxygen will not usually cause rapid oxidation, though slow union may occur, and proceed until almost complete without any appreciable rise of temperature; there is every reason to believe that even in these cases the oxidation of the substance really pro-

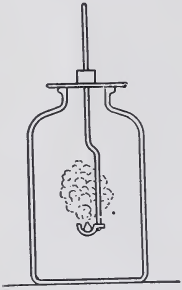

FIG. 6.—Phosphorus burning in Oxygen.

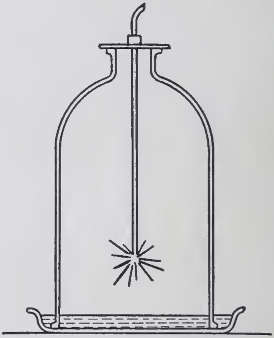

FIG. 7.—Steel Spring burning in Oxygen.

duces just as much heat as if it were rapid and an actual flame were produced; the heat is carried away by surrounding objects almost as fast as it is generated, thus preventing any perceptible rise of temperature. Generally it is necessary before active combustion, such as is usually called burning, will take place that the substance, or a portion of it, be heated to above a certain temperature in contact with oxygen. This particular temperature is called the *temperature of ignition,* and varies in the case of different substances between very wide limits. Thus, phosphuretted hydrogen ignites on contact with oxygen, even at the ordinary temperature, other substances, *e.g.,* carbon disulphide vapour, take fire when in contact with air at a comparatively low temperature, while others, which burn fiercely enough when ignited, *e.g.,* Marsh-gas, require a very high temperature for their ignition. The actual *ignition temperatures,* meaning by this term the temperatures at which rapid combustion commences, of several substances is given below:*

Phosphorus,	60° C.	=	140° F.	
Sulphur,	250°	=	482°	
Carbon disulphide,	149°	=	300°	
Acetylene,	480°	=	900°	
Charcoal,	350°	=	662°	according to the temperature at which the wood was charred.
	to			
	700°	=	1292°	

The first essential, then, with reference to combustion is that a portion of the combustible be heated to a sufficiently high temperature in contact with oxygen. But this is not sufficient to ensure complete combustion of the whole. If the substance is to continue to burn, it is necessary that the heat produced by the burning of one

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* The actual temperature of ignition is greatly influenced by external conditions, such as pressure, the nature of the walls of the containing vessel, etc. This is particularly the case with gases. (See also p. 104.)

portion should be sufficient to raise another portion of the substance to a temperature equal to or higher than the ignition temperature. Unless this be the case, the burning ceases. Thus it is evident why iron will not burn in air unless the heat produced by its own combustion be aided by some additional supply. The iron, when raised above the ignition temperature, begins to burn, but the heat evolved by its combination with oxygen is not sufficient, lessened as it is by that carried away by the nitrogen of the air, to raise another portion of iron to the temperature of ignition; the iron, therefore, unless it be aided by some external supply of heat, soon cools and ceases to burn.

Any agency which lowers the temperature of a flame may cool it so much that the temperature of the whole of the unburnt portion of the combustible is lowered below its ignition temperature. When this occurs the burning ceases and cannot recommence until the temperature of some portion of the combustible is again raised above the ignition point.

This fact is so important that it may be well to describe several experiments bearing upon it. A hot glass rod, not nearly red hot, will easily ignite the vapour coming from a little carbon disulphide placed on a porcelain dish, but is quite unable to ignite the vapour from ether under similar conditions.

If a short spiral coil or helix of copper wire be brought over the flame of a candle the flame will be extinguished, although the helix may have its coils sufficiently wide apart to not interfere greatly with the air supply; that this is due merely to the cooling effect of the copper may be shown by heating the wire to bright redness in a Bunsen flame and repeating the experiment, when, although some cooling effect will be produced, for the temperature of the red-hot wire is really much lower than that of the flame, still the amount of cooling will be much less than in the previous experiment, and it will be found quite impossible to extinguish the candle flame (Fig. 8).

Another experiment of a similar character may be performed by bringing a sheet of fine copper gauze over a tall gas flame; the latter will be depressed by the gauze almost as if by a solid sheet of metal (Fig. 9); the gas is not stopped by the gauze, but streams through and escapes, as may be proved by applying a light to the upper surface, when it will burn. The stoppage of the flame is due to the cooling effect of the gauze upon the mixed air and coal-gas, lowering their temperature below the ignition point. This action of wire gauze was discovered by Sir Humphrey Davy, and was applied by him in 1818 to the construction of a safety lamp for miners. The "Davy" lamp (Fig. 10) consists of an oil lamp, having its wick surrounded by a cylinder of wire gauze. Its

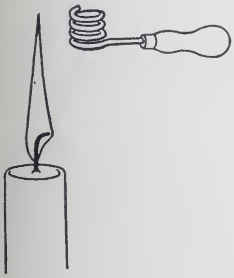

FIG. 8.—Helix and Candle Flame.

FIG. 9.—Action of Wire Gauze on Flame.

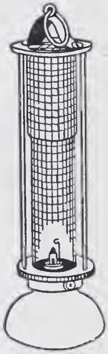

FIG. 10.—The Davy Lamp.

action depends upon the fact that when it is immersed in an inflammable mixture of firedamp and air, although the mixture may inflame and burn in the lamp, the flame cannot travel through the gauze, because the wire cools the gases below their ignition temperature. Thus the inflammation of the outside atmosphere by the lamp is prevented unless the gauze, by long heating, becomes so hot as to lose its specific cooling property, when the flame passes, and an explosion results. The gauze must be sufficiently fine. In practice it is found that gauze of 28 meshes to the linear inch yields the best results.

CHAPTER II.

EXPLANATORY.

Explanation of Chemical Terms—Outline of the Atomic Theory—Use of Chemical Formulæ and Equations—Short Glossary of Technical and Scientific Terms.

ALTHOUGH the use of purely systematic chemical phraseology will, as far as possible, be avoided, a limited acquaintance with the meaning attached to certain words by chemists is essential to a complete understanding of many of the processes with which we shall have to deal. It is proposed, therefore, in this chapter to define and explain many of the terms which will be employed in subsequent chapters.

ELEMENT.—By this term is meant a substance which, so far as can be ascertained, consists of but one kind of matter and resists all attempts to split it up into two dissimilar portions. Of such substances about 70 have been discovered, although by far the greater portion of all materials met with in ordinary life consist of combinations of comparatively few elements. The following is a list of elements, those of importance being printed in capitals.

LIST OF ELEMENTS WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

ALUMINIUM,	Al.	27.0	Neodymium,	Nd.	140.8
ANTIMONY,	Sb.	120.0	Nickel,	Ni.	58.7
Argon,	A.	39.0	Niobium,	Nb.	94.0
ARSENIC,	As.	75.0	NITROGEN,	N.	14.0
Barium,	Ba.	137.0	Osmium,	Os.	191.3
Beryllium,	Be.	9.1	OXYGEN,	O.	16.0
Bismuth,	Bi.	208.1	Palladium,	Pd.	106.3
Boron,	B.	11.0	PHOSPHORUS,	P.	31.0
Bromine,	Br.	80.0	PLATINUM,	Pt.	194.3
Cadmium,	Cd.	112.1	POTASSIUM,	K.	39.1
Caesium,	Cs.	132.9	Praseodymium,	Pr.	143.6
CALCIUM,	Ca.	40.1	Rhodium,	Rh.	103.0
CARBON,	C.	12.0	Rubidium,	Rb.	85.5
Cerium,	Ce.	140.3	Ruthenium,	Ru.	101.6
CHLORINE,	Cl.	35.5	Scandium,	Sc.	44.1
Chromium,	Cr.	52.3	Selenium,	Se.	79.0
Cobalt,	Co.	59.0	SILICON,	Si.	28.3
COPPER,	Cu.	63.4	SILVER,	Ag.	107.9
Erbium,	Er.	166.0	SODIUM,	Na.	23.0
Fluorine,	F.	19.0	Strontium,	Sr.	87.5
Gallium,	Ga.	69.9	SULPHUR,	S.	32.0
Germanium,	Ge.	72.3	Tantalum,	Ta.	182.5
GOLD,	Au.	197.2	Tellurium,	Te.	127.7
Helium,	He.	4.0	Terbium,	Tb.	126 (?)
HYDROGEN,	H.	1.0	Thallium,	Th.	204.2
Indium,	In.	113.7	Thorium,	Th.	232.4
Iodine,	I.	126.9	TIN,	So.	119.1
Iridium,	Ir.	193.0	Titanium,	Ti.	48.1
IRON,	Fe.	56.0	Tungsten,	W.	184.0
Lanthanum,	La.	142.3	Uranium,	U.	240.0
LEAD,	Pb.	206.9	Vanadium,	V.	51.4
Lithium,	Li.	7.0	Yttrium,	Y.	89.0
MAGNESIUM,	Mg.	24.3	Ytterbium,	Yb.	173.0
Manganese,	Mn.	55.0	ZINC,	Zn.	65.3
MERCURY,	Hg.	200.2	Zirconium,	Zr.	90.0
Molybdenum,	Mo.	95.7			

COMPOUND.—This word is also of very definite meaning. It refers to a substance containing two or more elements chemically united together in such a way that the properties of the compound substance bear no resemblance to those of any of its constituents. The same compound not only always contains the same elements, but it contains these in the same proportion. Moreover, the constituents of a compound are not only *mixed* together, they are chemically *combined.*

The differences between a chemical compound and a mere mixture are very marked, and it is highly important that a clear understanding be obtained of what these differences consist in.

Atom is a word very often used in every-day life, but usually in a very loose sense. The generally accepted *atomic theory* supposes all matter to be made of indivisible parts, which are called *atoms,* these atoms are indestructible and unalterable, they can pass from one state of combination to another, but they themselves remain unchanged, however numerous or violent the reaction in which they take part. Atoms, therefore, are necessarily *elementary* in their nature; phrases like "compound atom" or "atom of a compound substance" are obviously contradictions of terms and utterly meaningless. As a general rule the smallest portions into which we can subdivide any substance or into which we can conceive it to be subdivided, without altogether altering it, contain more than one atom. The smallest number of atoms, bound up together, which will produce a particle having all the characteristics of a substance, forms what is called a *molecule* of the substance. Molecules of substances, even of elements, generally contain two or more atoms, but some few elements (*e.g.,* mercury) seem to be capable of existing in the gaseous state in molecules, which contain only one atom. Molecules of compounds, of course, must contain at least one atom of each of their constituents; they, therefore, contain at least two, and may contain a very large number of atoms. All the atoms of any one element are alike in every respect; they, therefore, have the same weight, but the atoms of one element differ from those of another. What is the absolute weight of an atom of any element we cannot say, we only know that it must be exceedingly small, but we do know the relative weights of the atoms of different elements. Taking as the unit the $\frac{1}{16}$ of the weight of the atom of oxygen, a table of atomic weights can be constructed, which, though not giving the real weights of the atoms, gives their relative weights, and such a table serves many useful purposes in chemistry. (The table on page 18 gives the *atomic weights* of the elements on such a basis.)

To return to the consideration of the differences between a chemical compound and a mere mixture of two elements; if two substances be mixed, however thoroughly, the nature of the molecules is not altered; by sufficiently delicate means it is conceivably possible to discern molecules of one constituent lying side by side with those of the other. To take an extreme case, where the mixing can be made probably far more intimate and thorough than in the case of any solids, consider the mixture of two gases, say oxygen and hydrogen. In both these gases there is reason to believe that the molecules each contain two atoms, so that a mental picture of a space containing hydrogen gas would be something like Fig. 11. The molecules are, however, not at rest in a gas, but are continually moving to and fro, colliding with each other, and with the walls of the containing vessel. In the same way a space filled with oxygen gas may be conceived to be something like Fig. 12. The oxygen atoms, which are heavier than those of hydrogen, are distinguished in the figure by a central dot in the circles, the gas having a structure similar to that of hydrogen. If oxygen and hydrogen be mixed together, a mixture is obtained whose properties, *e.g.*, density, etc., are just what would be expected from the properties of its constituents. In accordance with the atomic theory, such a mixture would be constituted as represented in Fig. 13, some of the molecules being hydrogen, others oxygen.

This is typical of a mixture, and, as has been said, a gaseous mixture is probably far more intimate than any which could be made of two solids.

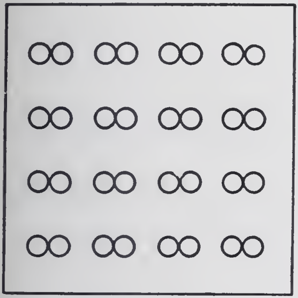

FIG. 11.—Space filled with Hydrogen.

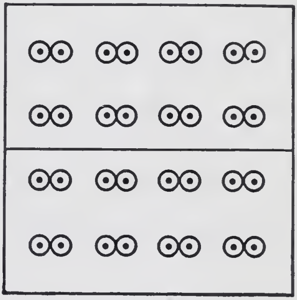

FIG. 12.—Space filled with Oxygen.

Now, if a *chemical compound* be formed of these two gases, as can be done easily by applying heat to the mixture, it will be noticed first of all, that there is a great outburst of heat and then that a new substance is formed, possessed of properties entirely different from those of both oxygen and hydrogen. The newly formed substance is water, and if it be kept in the gaseous state, *i.e.*, as steam (by keeping the temperature sufficiently high), it would probably have the structure depicted in Fig. 14. In this case new molecules are formed, each containing one atom of oxygen and two atoms of hydrogen. These cases may be taken as typical of the differences between chemical combination (resulting in the formation of a compound) and mechanical mixing (resulting in the formation of a mixture). In all cases of mere mixing, the molecules originally present in the constituents remain unchanged, and simply get intermingled, giving a body whose properties are the mean of its constituents, whereas in all cases where combination occurs new molecules are formed, with a consequently radical change in properties. Then, too, the *mixing* of two substances is not usually attended with any production or absorption of heat, but the *combination* of two substances is almost always accompanied by some thermal disturbance, generally by a rise of temperature.

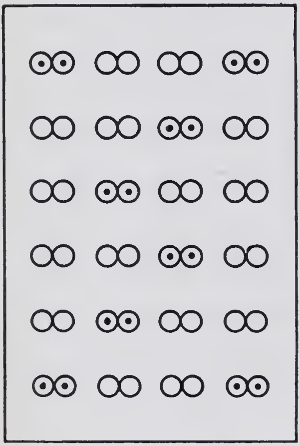

FIG. 13.—Space filled with Mixture of 2 Volumes of Hydrogen and 1 Volume of Oxygen.

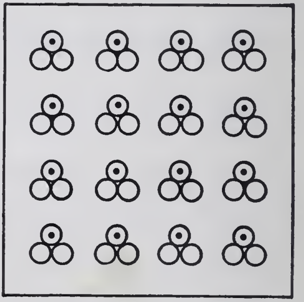

FIG. 14.—Space filled with Water Vapour.

Instead of confining our explanation to the theoretical aspect of the question, we might have, quite as efficiently, resorted to an experiment to explain the differences between a compound and a mixture.

If about 10 grammes of fine copper filings be mixed in a mortar with half their weight of sulphur, a dirty orange powder results. Under the microscope red particles of copper and lemon yellow fragments of sulphur can be distinguished lying side by side; moreover, by throwing some of this powder into water the constituents separate out according to their relative specific gravities, the copper particles sink to the bottom, while the lighter sulphur particles rest above the copper, or complete separation may be effected by treating a portion of the mixture with carbon disulphide, when the sulphur is removed in solution and the copper left. On allowing the carbon disulphide to evaporate, the sulphur is recovered in small crystals. In this case a *mere mixture* of sulphur and copper has been made, capable of separation by mechanical means and partaking of the properties of its constituents.

If some of the mixture be heated in a test-tube, chemical union between the copper and sulphur takes place attended by the production of heat and light, and there results a black substance totally unlike, in all its properties, either of its constituents. If this black substance be ground to powder and examined under the microscope, all the particles will be alike black in colour, and neither sulphur nor copper can be detected. If a portion of the mixture be treated with carbon disulphide, the substance is not changed in appearance, and the liquid, if filtered off, deposits on evaporation no sulphur (or at most a small trace, due to imperfect mixing or heating of the powder). Finally, if the powder be thrown upon water it all sinks together.

The substance is evidently neither copper nor sulphur, but by appropriate means it can be shown to contain both. If some of the powder be treated with strong nitric acid a violent action takes place, a dirty yellow mass floats on the top, and the liquid becomes blue in colour. If the liquid be diluted, filtered and brought into contact with a bright iron or steel blade, or some scrap zinc, a deposit of red, metallic copper will be obtained. If the dirty yellow residue be heated in air, it will burn with the blue flame and emit the characteristic odour of burning sulphur. The black substance obtained by heating the mixture of copper and sulphur is a *chemical compound* called sulphide of copper, and, like almost all compounds, was formed from its constituents with the evolution of heat.

In accordance with the atomic theory, chemists believe that chemical combination consists in a union of atoms of different elements, and the consequent formation of new molecules, and that the characteristic properties of a substance remain unchanged so long as its molecules are unchanged, but that directly any alteration of the molecules in a body takes place, a marked change in its properties is at once produced. Since chemical combination consists in union of the atoms of elements, and since these atoms have definite weights, it is clear that if the number of atoms of each element present in a molecule of a compound, and the weights of these atoms be known, the composition by weight of the substance may at once be ascertained. Thus, in the case of water, if a molecule of water contains, as it is practically known to do, one atom of oxygen united with two atoms of hydrogen, and if the relative weights of atoms of hydrogen and oxygen are 1:16, then it is evident that in 18 parts by weight of water there are 16 of oxygen and 2 of hydrogen.

Chemists express the composition of compounds by means of what are known as *formulae*. Every element has a *symbol* assigned to it, this being generally the initial letter of its name; in some cases, however, where there are several elements with the same initial, the initial letter is allotted to the most important element and a secondary letter is used with the same initial for the others.

(The symbols are given in the table on page 18.)

The symbols are used by chemists to write formulæ, by placing the symbols of the constituent elements of a compound side by side, and, if more than one atom of an element be present in the molecule, affixing a small figure to the symbol to indicate the number of atoms. If no figure be given, it is understood that one atom of the element only is present. Thus, the formula for water is written H_2O or OH_2, for ammonia, NH_3 or H_3N, etc.

Now a word or two as to the naming of compounds. A compound of two elements is named so as to indicate the two elements present; the name of one element (the metal, if one be present) is used in full, and the name of the other is changed so as to end in -ide; thus potassium and chlorine form a compound KCl, which is called potassium chloride; barium and oxygen form barium oxide, and so on.

Sometimes an element will unite with another in several different proportions; thus carbon unites with oxygen in the proportion of 12 to 16 and 12 to 32, or, in formulæ CO and CO_2, the former is called carbon monoxide, the latter, carbon dioxide; sulphur and oxygen form SO_2 and SO_3, sulphur dioxide and sulphur trioxide respectively, the prefixes mono-, di-, tri-, meaning one, two and three; so in the same way, tetra- (four), penta- (five) and hexa- (six) are sometimes used to indicate the number of atoms present of the element to whose name they are prefixed.

There are other ways of naming compounds in use, but reference must be made to any modern text-book of systematic chemistry for additional information as to chemical nomenclature.

Chemists are in the habit of expressing not only the composition of substances, but also chemical changes, by the aid of formulæ; this they do by writing what are called *chemical equations.* In such equations the formulæ of the substances which are to act upon each other are connected by the sign +, and placed on one side (the left) of the sign =, and the formulæ of the products are placed on the other (right hand) side, such numbers of molecules being taken as shall make the equation true in an ordinary mathematical sense.

Take a simple case, the burning of carbon in air or oxygen (in either case the chemical change is the same, the formation of carbon dioxide):

$$\underset{\text{Carbon}}{C} \quad + \quad \underset{\text{Oxygen}}{O_2} \quad = \quad \underset{\text{Carbon dioxide}}{CO_2}.$$

O_2 is written instead of $2\ O$ to represent the fact that the molecule of oxygen contains two atoms; $2\ O$ would mean two atoms not combined together. Another less simple example is the following:

$$\underset{\text{Sodium}}{2\ Na} \quad + \quad \underset{\text{Water}}{2\ H_2O} \quad = \quad \underset{\text{Caustic soda}}{2\ NaOH} \quad + \quad \underset{\text{Hydrogen}}{H_2}.$$

This means that 2 atoms of sodium acting upon 2 molecules of water produce 2 molecules of sodium hydroxide, and 1 molecule of hydrogen.

A chemical equation should be like an algebraical equation in that the sum of the atoms of each element on one side are equal to those on the other, but it is not like an algebraical equation in that it is not necessarily reversible, *i.e.,* the reaction, which would be indicated by the equation written in the opposite way, may not be capable of being realised in practice.

GLOSSARY OF SOME OF THE TERMS USED IN THE FOLLOWING CHAPTERS.

ACID.—A substance possessing a sour taste and the property of changing vegetable blues, *e.g.*, litmus, to red and containing hydrogen which can be replaced by a metal. Many of the strong mineral acids, *e.g.*, sulphuric or nitric acid, are possessed of powerful corrosive properties upon metals, organic matter, etc. A substance is said to have an *acid reaction* if it fulfils the first two clauses in the above definition.

ALKALI.—A substance opposed in its properties to an acid, capable of neutralising and destroying the characteristic properties of an acid, forming therewith a salt and usually water. The most important alkalies are soda, $NaOH$; potash, KOH, and lime, CaO or $Ca(OH)_2$. Ammonia, NH_3, or in solution probably NH_4OH, also acts as an alkali. A substance is said to have an *alkaline reaction* if it turns vegetable colouring matters, *e.g.*, litmus, which have been turned red by acids back to blue again.

BACTERIA.—A general name for the smallest known living organisms, including bacilli (rod-like), micrococci (spherical), and spirilla (spiral or corkscrew-like), these names being descriptive of their form. They are plants,* being in some respects like the fungi, and multiply with great rapidity. They are exceedingly abundant, occurring everywhere around us, in the air, in water and in the soil. Many play an important part in putrefaction, others in diseases. As a rule, they lose their activity at the freezing point, but regain it at a more genial temperature. They are killed by exposure to the temperature of boiling

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* Opinions differ on this point, especially with regard to the motile bacilli.

water; the spores of some, however, can resist for a short time even this high temperature.

Destructive Distillation.—The change produced when a substance, generally organic, is submitted to a high temperature and evolves gases and vapours formed by the decomposition of the original body, it being permanently destroyed by the process. A good example is seen in the preparation of gas from coal.

Endothermic and Exothermic Bodies.—These terms are almost explained in the text. (See Chap. VIII., page 132.) By an Exothermic body is understood a substance in whose formation heat was evolved. Most substances are exothermic. An Endothermic body, on the other hand, is one in whose formation heat was absorbed. Consequently, to decompose an exothermic compound heat or energy is required, while in the decomposition of an endothermic substance heat is evolved. The latter, therefore, are generally unstable and often explosive.

Microbe.—Another name for bacterium.

Micro-Organism.—Any minute form of life, including microscopic animals and plants. Used in a wider sense than bacterium or microbe.

Organic Matter.—Strictly speaking, matter which has been produced by organisms, *i.e.*, by living beings, but used in a chemical sense for any compound of carbon, whether formed by life processes or artificially. Almost all organic matter, when heated out of contact with air, blackens, owing to the separation of carbon; with free access of air, combustion occurs and carbon dioxide, with other products, is formed.

Oxidising and Reducing Agents.—By oxidation is meant union with oxygen, but in a chemical sense the term is given a wider significance, viz., that the element which undergoes "oxidation" is caused to combine with a larger amount of oxygen or some substance playing the part of oxygen, *e.g.*, the conversion of stannous chloride, $SnCl_2$, into stannic chloride, $SnCl_4$, is called by chemists a process of oxidation, though no oxygen may be concerned in it. Reduction is used in exactly the opposite sense. A substance which brings about oxidation is said to be an "oxidising agent," while one which removes oxygen is called a "reducing agent." Common oxidising agents are nitric acid and nitrates, chlorates, chlorine, etc., while reducing agents are represented by easily oxidisable metals (*e.g.*, zinc), sulphurous acids or sulphites, etc.

PUTREFACTION.—A process of decomposition of organic matter produced by the life action of bacteria or other micro-organisms, *e.g.*, yeast, mould, etc., often accompanied by oxidation by the air, in which case heat is produced.

SALT.—A substance derived from an acid by the substitution of a metal for the whole or part of the hydrogen. A salt is formed when an acid acts upon an alkali or base, and is often (incorrectly, according to modern views) spoken of as containing an acid and a base.

SATURATED AND UNSATURATED COMPOUNDS.—These terms are generally applied to organic compounds, and indicate whether the proportions of atoms of carbon to atoms of hydrogen or other element correspond to a certain value or is above that value. For example, in the hydrocarbons, carbon is able to unite with hydrogen in the ratio expressed by the formula C_nH_{2n+2} and no compound containing a greater ratio of hydrogen to carbon than this is known; such hydrocarbons are therefore said to be saturated. Hydrocarbons of the general formula

C_nH_{2n} and C_nH_{2n-2} are also known, obviously not containing so great a ratio of hydrogen to carbon as the first-mentioned class, and, therefore, capable of uniting with more hydrogen or other element; such compounds are said to be "unsaturated." The terms applied to the fatty acids have a similar meaning; stearic acid, $C_{18}H_{36}O_2$, is an example of a saturated acid, while oleic acid, $C_{18}H_{34}O_2$, is unsaturated. Or, more generally, acids of the formula $C_nH_{2n}O_2$ are saturated, while those corresponding to $C_nH_{2n-2}O_2$ and $C_nH_{2n-4}O_2$ are unsaturated.

VOLATILE.—Capable of being converted from a liquid or solid into gas or vapour by heat. The term is used in two senses:

(1) When a substance on heating is converted into vapour or gas without undergoing chemical change. In this case the vapour on being cooled is transformed again into the original liquid or solid, *e.g.*, water, camphor.

(2) When a substance, on being heated, is converted into gases or vapours and at the same time chemical change, either decomposition or oxidation, takes place. In this case the body is permanently altered, and on cooling the vapours or gases do not yield the original substance.

CHAPTER III.

OXYGEN.

Methods of Preparation of Oxygen—Oxygen Manufacture—Heat Measurements—The Calorimeter—Calorific Power of Substances Burning in Air.

SOME of the properties and one of the methods of preparation of oxygen have been already (Chap. I.) briefly described. In this chapter the methods generally used for the preparation of oxygen on the large scale, and further phenomena attending combustion, will be considered.

By the student in a chemical laboratory oxygen is usually obtained by the action of heat upon a white crystalline substance known as potassium chlorate. This substance contains potassium, chlorine and oxygen, and when heated evolves its oxygen, leaving behind a compound containing only potassium and chlorine, and known as potassium chloride.

$$\underset{\text{Potassium chlorate}}{2\,KClO_3} \quad = \quad \underset{\text{Potassium chloride}}{2\,KCl} \quad + \quad \underset{\text{Oxygen.}}{3\,O_2}$$

The operation is usually carried out in a glass flask provided with a cork and tube to lead the gas evolved into a bottle or jar filled with water and placed in a pneumatic trough (Fig. 15). An addition of manganese dioxide to the potassium chlorate causes the latter to decompose at a lower temperature and without previous fusion.

On the large scale, oxygen is obtained from some cheap raw material. The cheapest material that could be used is the air, and this is the source from which the oxygen, now an important commercial product, is obtained. The method of its preparation depends upon certain peculiar behaviour of a substance known as barium oxide or sometimes, as baryta.

This substance, when heated to about 600° C. (1112° F.), at the ordinary pressure, or to 700° C. (1292° F.) under greater pressure in contact with oxygen, or any mixture containing oxygen, absorbs that gas and forms a substance containing twice as much oxygen as the original barium oxide. To indicate the composition of the new compound chemists call it barium dioxide, the original barium oxide being, strictly speaking, barium monoxide.

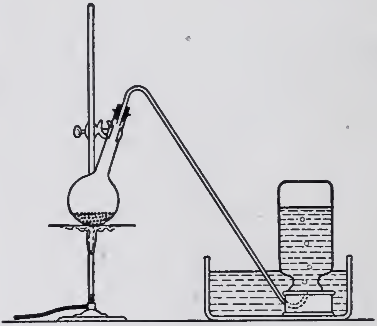

FIG. 15.—Preparation of Oxygen from Potassium Chlorate.

The barium dioxide on heating to a slightly higher temperature (about 850° C. [1560° F.], or even at the same temperature 700°-750° C., if the pressure of the gas above it be diminished) splits up readily into oxygen, which comes off as a gas, and barium monoxide again.

Represented in the form of an equation, the reactions are written as follows:

$$(1)\ 2\,BaO + O_2 = 2\,BaO_2.$$
$$(2)\ 2\,BaO_2 = 2\,BaO + O_2.$$

The manufacture of oxygen by this method as carried out on the large scale is known as Brin's process.

Air, dried and freed from carbon dioxide, is pumped under pressure (about one atmosphere additional) into a series of vertical steel cylinders containing barium oxide, and heated by a gas furnace to about 750° C.; the oxygen is absorbed, forming barium dioxide, while the nitrogen escapes into the outer air. After a few minutes the supply of air is shut off, and the cylinders are connected with a series of exhaust pumps, whereby the nitrogen remaining in the apparatus is first removed and the pressure thereby diminished to 2 or 3 inches of mercury. The barium dioxide, under these circumstances, begins to decompose, reforming barium monoxide and evolving oxygen, which is removed by the pumps as fast as it forms, afterwards compressed by powerful force-pumps, and sent into the market in the compressed state in steel cylinders* (Fig. 16) which contain the gas under a pressure of from 100-150 atmospheres, *i.e.*, from 1500-2000 pounds on the square inch.

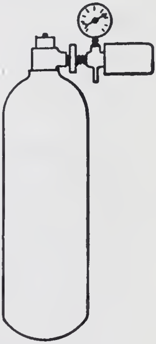

Fig. 16.—Cylinder for Compressed Gas, showing Gauge and Reducing Valve.

The gas so obtained is about 96% oxygen, the commercial product as sent into the market containing over 90% of oxygen.

Many other methods of preparing oxygen on the

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* The whole cycle of operations takes about 10 minutes.

large scale have been proposed; only one of them, so far as we know, can compete with Brin's process. This is a process originally devised by Tessie du Motay many years ago (1866), and which has recently been revived.* This process, like the Brin's, uses the air as the source of oxygen. A mixture of manganese dioxide and caustic soda is heated in a current of air, oxygen is absorbed, forming sodium manganate, and nitrogen passes on and is allowed to escape. The sodium manganate is afterwards heated in a current of steam, when caustic soda and manganese dioxide are again formed and oxygen is liberated.

The reactions are expressed by the following equation:

$$\underset{\substack{\text{Caustic}\\\text{soda.}}}{4\,\mathrm{NaOH}} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{2\,\mathrm{MnO_2}} + \underset{\substack{\text{Oxygen}\\\text{from air.}}}{\mathrm{O_2}} = \underset{\substack{\text{Sodium}\\\text{manganate.}}}{2\,\mathrm{Na_2MnO_4}} + \underset{\text{Water.}}{2\,\mathrm{H_2O}}.$$

On heating in a current of steam, the above reaction is practically reversed. The changes occur at a low temperature, 320°-430° C. (608°-806° F.). The oxygen produced by this process is very pure (95%) and can be transported by compressing it into cylinders, exactly as in the case of the Brin's oxygen.†

A very ingenious method of preparing oxygen from air has been proposed by Prof. Linde, of Munich.‡ This method is a purely mechanical one. Air is forced, under considerable pressure, into a long pipe, the front portion of which is kept cool by a water-jacket. This removes the heat produced by compression, and the air, cooled down to ordinary temperature, passes on. The

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* Fanta, *Jl. Soc. Chem. Indus.*, 1892, p. 312.

† Quite recently, Stuart has introduced a modification in this process, viz., the use of sufficient excess of caustic soda to give fusibility to the whole. By this means the process is said to be greatly cheapened (*Jl. Soc. Chem. Indus.*, 1899, p. 293).

‡ *Jl. Soc. Chem. Indus.*, 1895, p. 984; and *Engineer*, Oct. 4, 1895, p. 325.

farther end of the pipe is surrounded by a wider tube, through which passes the air, after it has been allowed to escape from the end of the inner pipe, and consequently to expand. In expanding it absorbs as much heat as it gave out in being compressed, and since that heat was removed by the water-jacket, it cools itself and the inner tube far below the temperature of the air. As the process goes on, a lower and lower temperature is attained, until finally the air in the inner pipe begins to liquefy, owing to its very low temperature. If this liquid air be allowed to evaporate, the nitrogen boils off more rapidly than the oxygen, and we thus get a residue containing about 80% of oxygen. This process is, we believe, not yet in operation on the large scale, but may be of importance in the future.*

Properties of Oxygen.—The gas is colourless, odourless and tasteless. It is slightly heavier than air, its specific gravity (that is, the weight of any volume compared with that of the same volume of air) being 1.1049. One thousand cubic feet of oxygen at 32° F. and at a pressure of 30 inches of mercury weighs 88.9 pounds. The gas is only slightly soluble in water, though its solubility is greater than that of nitrogen; 100 volumes of water absorb about 4 volumes of oxygen and about 2 volumes of nitrogen. By strong cooling, aided by pressure, oxygen can be liquefied; it then becomes a bluish liquid of specific gravity about 1.0 and boiling at — 180° C. (—292° F.). As has been seen (Chap. I.), oxygen is chiefly remarkable for the readiness with which it enters into combination with other substances. The act of combination evolves light and heat, and takes place in almost all instances of combustion.

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* For an account of possible applications of this process see abstract of a paper by Hempel (*Jl. Soc. Chem. Indus.*, 1899, p. 121).

It has been already stated that the total quantity of heat evolved by the union of a given weight of any particular substance with oxygen is the same, however the combination be effected. It may be well here to say a few words about the measurement of heat. The use of a thermometer as a measurer of *sensible heat* or *temperature* is familiar to every one, but to measure a *quantity of heat* requires a further knowledge of the subject.

In measuring quantities of heat, it is necessary, as in all measurements, to fix upon some unit, and in this case it is the quantity of heat necessary to raise the temperature of 1 pound of water through 1° F., or 1 gramme through 1° C. This quantity is called the *thermal unit* or *unit of heat;* in the case of 1 gramme being taken as unit of weight, the thermal unit is called the *calorie.* This term is also applied to the quantity of heat necessary to raise the temperature of 1000 grammes or 1 kilogramme of water through 1° C. In order to prevent confusion, the larger unit is written with a capital letter, *Calorie.* Now it is found that it requires more heat to raise the temperature of 1 pound of water through 1° F. than it does to raise 1 pound of any other substance through 1°. This is expressed by saying that the *specific heat* or *capacity for heat* of water is greater than that of any other chemical compound. The specific heat of water is taken as unity, hence the specific heat of a substance is the number of units of heat required to raise the temperature of the unit weight of the substance through 1° C. or F. The number, which is nearly always less than 1, will be the same, whether we take as our unit the pound, the gramme or the kilogramme.

The following table gives the specific heats of a number of substances:

Water	1.000	Glass	.198
Alcohol	.620	Steel	.118
Ether	.516	Brass	.094
Turpentine	.426	Aluminium	.214
Glycerine	.555	Lead	.031
Carbon disulphide	.245	Copper	.094
Sulphuric acid	.355	Tin	.056

Instruments used for measuring quantities of heat are called *calorimeters.* In its simplest form a calorimeter consists of a vessel containing a known quantity of water, and so constructed that the escape of heat, either out of or into the water, from external sources is, as far as possible, prevented. If any quantity of heat is to be measured, it is so arranged that the heat shall flow into the water, when the rise in temperature which that liquid undergoes, together with the weight of the water, after certain corrections for the heat taken by the walls of the vessel itself and the thermometer, give at once a means of measuring the amount of heat (Fig. 17).

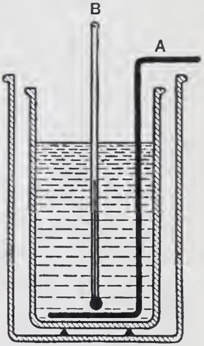

FIG. 17.—Simple Form of Mixture Calorimeter. A, the Stirrer; B, the Thermometer.

By the use of a calorimeter so planned that all the heat evolved by the combustion of a known weight of a substance in oxygen or air shall be absorbed by the water, a number called the *heat of combustion* of the substance can be calculated. This expresses the number of units of heat evolved by the combustion of 1 unit of weight of the substance. The heat of combustion of a substance is sometimes called its *calorific power.* In pure science we always use the Calorie or calorie as the unit (*i.e.,* heat required to raise 1 kilogramme or 1 gramme through 1° C.), but among engineers, etc., in this country the so-called *British unit of heat* is employed (the heat required to raise 1 pound of water from 39° to 40° F.). The two units are connected thus: 1 Calorie = 1000 calories = 3.97 (say 4) British units, or 1 British unit = 0.252 Calorie = 252 calories.

The following table gives the *heats of combustion or calorific power* of several substances with oxygen, *i.e.*, the numbers of calories evolved by the combustion of 1 gramme of the substance:

Charcoal	8,080	Air-dried wood	2,800
Hydrogen	34,460	Charred wood	3,600
Sulphur	2,220	Dried peat	4,800
Phosphorus	5,747	Average coal	7,500
Marsh-gas	13,060	Good coke	7,050
Carbon monoxide	2,400		

We repeat that it makes no difference to the *amount of heat*, though it does to the temperature, whether the combustion takes place in air or in pure oxygen. The heat of combustion is the same in both cases. The temperature attained by a fuel is sometimes called the *Calorific Intensity.*

There are one or two other considerations about heat which may be introduced here.

Suppose water at the ordinary temperature be taken, and heat applied to it, we can tell by means of a thermometer what becomes of the heat, the temperature of the water rises and in exact proportion to the quantity of heat added. In other words, every unit of heat produces its effect in raising the temperature of a pound or kilogramme 1 degree, or any other quantity a proportionate amount. This would go on almost regularly until the thermometer stood at 100° C. (212° F.). No further rise in temperature would occur, and even if twice or thrice the supply of heat previously employed were applied no effect upon the thermometer would be produced.

If the thermometer be removed from the water and its bulb surrounded by the steam arising therefrom, it will be noted that the temperature of the steam is likewise 100° C. The heat which then enters the water becomes hidden or latent, as it is called. The only change that occurs is that liquid water becomes gaseous water, or, in other words, the water is converted into steam. Water at a temperature of 100° C. and steam at 100° C. exist together in the same vessel, and evidently water, in changing into steam, absorbs heat, though no rise in temperature is produced. A very large amount of heat is thus consumed. To convert 1 pound of water at 100° C. into steam at 100° C. requires, in fact, as much heat as would raise the temperature of 536 pounds of water from 0° to 1° C. (or 965 pounds from 32° to 33° F.) *i.e.*, 536 units of heat. This number, 536, is called the *latent heat of steam* or the *latent heat of vaporisation of water.*

Every liquid in changing into a gas or vapour requires a considerable quantity of heat. There are numbers of illustrations familiar to all which confirm this statement. If we wet our hand and expose it to the air evaporation takes place, and a marked sensation of cold is produced. If a more volatile liquid than water, *e.g.*, ether, be used the evaporation takes place more rapidly and the cooling effect is more marked. By means of a spray of ether, driven by a blast of air, very considerable cooling can be effected, *e.g.*, water can be frozen. Advantage of the cooling effect of evaporation is often taken for the purpose of cooling wines and for freezing water. In the former case a common practice is to wrap the wine bottle in a wet cloth and suspend it in a current of air. The wind causes the evaporation of the water to take place rapidly, and consequently heat is absorbed by the water; this heat is abstracted, first from the water itself, and then from the wine. In the case of freezing machines, the cooling effect used is the rapid evaporation of some very volatile liquid, *e.g.*, ether or liquid ammonia.

Conversely, when a vapour or gas becomes a liquid, heat is given out. The amount given out is exactly equal to the amount absorbed when the liquid became a gas.

The *latent heat of vaporisation* of a substance, then, is the quantity of heat which is absorbed when the unit weight of a liquid is converted into a gas, or the quantity which is evolved when the unit weight of a gas becomes a liquid.

There is another change of state when a liquid solidifies, or when a solid liquefies; in this case, too, evolution or absorption of heat is observed. The *latent heat of fusion* is, as might be expected, generally much less than the latent heat of vaporisation; in the case of water it is about 80; that is, a pound of ice at 0° in melting to water at 0° C. absorbs as much heat as would raise the temperature of 80 pounds of water from 0° to 1° C., or 144 pounds from 32° to 33° F. So, also, to convert 1 pound of water at 0° C. into ice at 0° C. it is necessary to remove 80 times as much heat as would raise 1 pound of water 1° C., or 144 times as much as would raise it 1° F. The reason ice forms only slowly during frost, and also the advantage of using crystallised salts (which melt in their water of crystallisation), *e.g.*, sodium acetate instead of hot water in foot-warmers in railway carriages, now become apparent. In both cases the latent heat of fusion is given out during solidification, and enormously prolongs the time of cooling by increasing very greatly the total amount of heat which has to be removed in order to reduce the temperature through any definite interval.

The latent heats of fusion and vaporisation of water are exceptionally high, as compared with most other substances.

Substance.	Latent Heat of Vaporisation.	
	Fahr.	Cent.
Water	965	536
Acetic acid	183.6	102
Ether	162	90
Carbon disulphide	156.6	87

Substance.	Latent Heat of Fusion.	
	Fahr.	Cent.
Water	142.6	79.2
Sulphur	16.87	9.37
Phosphorus	9.09	5.03
Mercury	5.09	2.83

Having now explained some of the more important points connected with the heating effect of combustion, and in a previous chapter alluded to some conditions which regulate its occurrence, we shall next refer very briefly to certain phenomena which are apparently exceptions to the general statements already made.

It is, as a general rule, necessary in order to make a substance burn, that a portion of the substance should be heated to its temperature of ignition. Apparent exceptions are to be met with where a substance whose temperature of ignition is moderately high will, under certain conditions, burst into flame when brought into contact with air at a very much lower temperature. Finely divided combustible substances will often do this. For example, if metallic iron, obtained by gently heating oxalate of iron in a current of hydrogen, be projected into the air it will ignite and oxidise with incandescence. So, too, if phosphorus dissolved in carbon disulphide (which solution is sometimes known as "Fenian fire") be poured on to a piece of paper, as soon as the carbon disulphide has evaporated, the finely divided phosphorus crystals which remain will ignite when they become dry and will often set fire to the paper.

As might be expected, it is found that anything which tends to favour more intimate contact between the combustible and air tends to promote combustion and to lower the temperature of ignition. It may be, and, indeed, in many cases probably is, that the lowering of the temperature of ignition is only apparent, that the fineness of division, etc., really increases the rate of slow oxidation, which goes on in so many cases before actual ignition occurs, and thus tends to raise the temperature of the body by the heat so generated, up to the actual ignition point. In the same way, a very porous state of a combustible is always favourable to its oxidation, and sometimes may lead to its ignition without the aid of any external source of heat. Thus, freshly burnt charcoal, which is highly porous, will, on free exposure to air, often take fire. It is only fair to add that mere increase of surface of contact is not the only cause of this spontaneous combustion; it is probably due largely to a property possessed by charcoal of condensing in its pores, or *occluding*, as it is called, many gases, amongst others oxygen, and this condensation, like all condensation of gases or vapours, evolves heat, which favours slow oxidation. In time this develops so much heat that the temperature of ignition is actually reached and the charcoal bursts into flame.

A similar power of occluding gases is possessed by metallic platinum, when in the form of sponge. In this case the substance is not inflammable, and it cannot, therefore, burn itself. If, however, hydrogen, a very inflammable gas, be brought into contact with the spongy platinum, which contains oxygen from the air in its pores, a condensation of hydrogen also takes place, and the two gases are brought into such intimate contact in the pores of the platinum that combination occurs, great heat is evolved (the platinum becomes red hot) and the hydrogen is ignited. Upon these facts, discovered many years ago, Döbereiner based his formerly well-known lamp, which can be used for the production of a flame. The lamp (Fig. 18) consists essentially of an apparatus for generating hydrogen by the action of zinc upon dilute sulphuric acid; the jet of hydrogen is directed upon a little platinum gauze basket containing spongy platinum. The lamp is so constructed that it always contains a store of hydrogen, which issues at once from the jet when the stop-cock is turned, the jet blows upon the spongy platinum, some of the hydrogen condenses and quickly raises the temperature of the platinum to redness, this ignites the jet of hydrogen, producing a non-luminous but intensely hot flame, from which a taper or other combustible may be ignited. On closing the stopcock, the acid is blown from the zinc, the action stops, and the apparatus is left ready for use again.

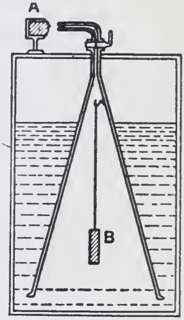

FIG. 18.—Döbereiner Lamp. A, Spongy Platinum; B, Rod of Zinc. The Liquid is Dilute Sulphuric Acid.

Many substances undergo slow combustion when exposed to oxygen or air, this combustion produces heat, and although perhaps in many cases no appreciable rise in temperature may be recognised, heat, in proportion to the amount of the body oxidised, is always evolved. If the conditions are favourable to oxidation, *e.g.*, if a very large surface of the combustible be exposed to air, and especially if the loss of heat by conduction, etc., be impeded, *e.g.*, if too free access of fresh cold air be prevented, then an appreciable rise of temperature may take place, in some cases sufficiently great to bring about rapid oxidation and actually to set fire to the material. This often occurs when drying oils are spread over a large surface by being soaked up in cotton waste and left in heaps undisturbed. The heap will in many cases burst into flame, especially if it be in a warm place, as near a steam or hot-water pipe. (See under oils.)

CHAPTER IV.

COAL-GAS.

Its Preparation, Purification and Composition—Properties of Its Chief Constituents—Reciprocity of Combustion—Gaseous Diffusion—Gaseous Explosions—Dust Explosions.

The part played by the oxygen of the air in combustion having been explained, it is proposed in this chapter to devote some time to a consideration of the method of preparation and principal properties of what is still the most commonly used gaseous combustible—coal-gas.

Coal consists of the remains of vegetable matter which have undergone numerous changes, some in chemical composition, by fermentative processes, probably under or at least in the presence of water, some in physical state, produced by the pressure of the strata deposited above.

Coal varies in composition and properties; a general idea of its chemical character may be gleaned from Table I.

When coal is heated in air it inflames and *burns, i.e.,* unites with oxygen, forming chiefly carbon dioxide and water vapour, and leaving behind an ash which varies greatly in amount (from 1% to 40% on the whole coal) and somewhat in composition. Coal ash always contains alumina, silica, oxide of iron, lime, sulphuric acid and a trace of phosphoric acid.

TABLE I.

Name of coal.	Carbon.	Hydrogen.	Nitrogen.	Oxygen.	Sulphur.	Ash.	P'rc't'ge of coke left.
Merthyr (Welsh)	90.9	4.3	1.2	0.9	1.2	1.5	85.0
Pontypool (Welsh)	80.7	5.7	1.4	4.4	2.4	5.5	65.0
Newcastle (Hartley)	81.8	5.5	1.3	2.6	1.7	7.1	64.6
Broomhill (Newcastle)	81.7	6.2	1.8	4.4	2.9	3.1	59.2
Loscoe, soft (Derby)	77.5	4.9	1.6	12.4	1.3	2.3	52.8
Wigan (Cannel)	79.2	6.1	1.2	7.2	1.4	4.8	50.3
Grangemouth (Scotch)	79.9	5.3	1.4	8.6	1.4	3.5	56.6
Barnsley ("Hard")	80.0	4.9	2.2	10.0	1.1	1.8	61.7
Silkstone (Yorks)	79.0	5.2	1.5	6.0	1.5	2.8	...

When coal is distilled in closed vessels, it yields many products, which divide themselves into three classes:

(1) *Solids,* which remain in the retort—coke.

(2) *Liquids,* which are condensed by cooling—tar and ammonia liquor.

(3) *Gases.*

The coal used for the preparation of coal-gas is either coking coal or cannel, the latter yielding a gas possessing a very high illuminating power. Newcastle and Silkstone coals are much prized for gas-making. Cannel is often used with bituminous coals, so as to yield a gas richer in illuminating constituents than could be obtained from bituminous coal alone. The yield of gas varies with the method of distillation and with the coal used. It is usually from 10,000 to 12,500 cubic feet per ton of coal distilled.

The distillation is generally effected in horizontal retorts having a D-shaped section, and these are charged at one end by means of a door, or, in more recent forms, from both ends. The retorts are made of either fire-clay or iron, and are heated sometimes by coal, but better by gaseous fuel (producer gas). From the retort the gas and vapours expelled from the coal (being produced in it by the heat to which it is submitted) pass upwards through an iron pipe, which is then bent downwards and dips into a large horizontal pipe kept half filled with liquid. The end of the pipe from the retort dips beneath the liquid in this "hydraulic main," as it is called, and shuts off communication between the retort and the further apparatus, so as to prevent escape of gas when the former is opened for recharging. (See Fig. 19.)

A considerable quantity of the liquid products condense and collect in the hydraulic main, and the rest is removed by passing the gases through a series of tall iron pipes, up and down which they have to travel, and where they are cooled. By ascending a tower, filled with coke, down which water trickles ("scrubber"), ammonia and other gases soluble in water are removed. The gases then pass into the "purifiers," where they are deprived of carbon dioxide (CO_2) and sulphuretted hydrogen (H_2S), two objectionable ingredients which are always formed when coal is distilled. Another sulphur compound, carbon disulphide (CS_2), is usually present and is here removed. Two substances are used in the purifiers: sometimes slaked lime, often spread over a large surface by mixing with sawdust; in this case the reactions by which the purifications are effected are:

$$\underset{\text{Lime.}}{CaH_2O_2} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} = \underset{\substack{\text{Calcium}\\ \text{carbonate.}}}{CaCO_3} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\text{Lime.}}{CaH_2O_2} + \underset{\substack{\text{Sulphuretted}\\ \text{Hydrogen.}}}{H_2S} = \underset{\substack{\text{Calcium}\\ \text{Sulphide.}}}{CaS} + \underset{\text{Water.}}{2\ H_2O.}$$

$$\underset{\text{Lime.}}{CaH_2O_2} + \underset{\text{Sulphuretted hydrogen.}}{2\ H_2S} = \underset{\text{Calcium hydrosulphide.}}{CaH_2S_2} + \underset{\text{Water.}}{2\ H_2O.}$$

$$\underset{\text{Calcium hydrosulphide.}}{CaH_2S_2} + \underset{\text{Carbon disulphide.}}{CS_2} = \underset{\text{Calcium thio-carbonate.}}{CaCS_3} + \underset{\text{Sulphuretted hydrogen.}}{H_2S.}$$

In other cases a hydrated oxide of iron, "bog ore," is used when—

$$\underset{\text{Hydrated oxide of iron.}}{Fe_2O_3.H_2O} + \underset{\text{Sulphuretted hydrogen.}}{3\ H_2S} = \underset{\text{Sulphide of iron.}}{Fe_2S_3} + \underset{\text{Water.}}{4\ H_2O.}$$

When the hydrated oxide of iron has thus become converted into sulphide of iron, or "fouled," it has lost its power of removing sulphur compounds from the gas. It is then "revivified" by the simple expedient of exposing it to air, when oxygen is absorbed and sulphur set free, as in the following equation:

$$\underset{\text{Iron sulphide.}}{2\ Fe_2S_3} + \underset{\text{Oxygen.}}{3\ O_2} = \underset{\text{Iron oxide.}}{2\ Fe_2O_3} + \underset{\text{Sulphur.}}{6\ S.}$$

The mixture of re-formed oxide of iron and sulphur is then again placed in the purifier, and again is able to absorb the sulphuretted hydrogen. This process of fouling and revivification can be repeated 12 or 16 times, when the sulphur accumulates so that it forms about 55% of the total mass. It is then used for making sulphuric acid. A small quantity of air or, better, oxygen, is sometimes admitted into the purifier along with the coal-gas in order to make the process of revivification continuous.

One phenomenon in connection with this purification by means of hydrated ferric oxide is of interest, it is found that the heat produced by the "revivification" is sometimes so great that the sulphur is actually ignited;

the mass, therefore, on exposure to air may spontaneously inflame.

After purification the gas is stored in large gasholders, made gas tight by water.

Now, as to the chemical nature of coal-gas; analysis shows it to be a complex mixture of gases, the following being the main constituents and proportions by volume:

		Per cent.
Hydrogen	about	50
Marsh-gas	"	33
Carbon monoxide	"	6 to 11
Heavy hydrocarbons	"	3 to 11
Oxygen, nitrogen, carbon dioxide		traces

Of these gases, as will be seen later, the first three, the most abundant, although they are inflammable and evolve considerable heat by their union with oxygen, give, in burning, practically no light. It is to the presence of the substances called "heavy hydrocarbons" in the above table that the luminosity of a coal-gas flame is due. The chief constituent of this class of bodies is *ethylene,* whose properties may be briefly described.

Ethylene is a colourless gas, slightly lighter than air, capable of burning with a luminous, smoky flame, forming when completely burnt carbon dioxide and water, though usually a considerable amount of the carbon escapes combustion and is evolved as soot. When heated alone, ethylene is decomposed with separation of carbon and formation of simpler hydrocarbons, especially Marsh-gas. It is to this circumstance that the illuminating power of ethylene and its importance in coal-gas are due, the fine particles of separated carbon being heated to whiteness in the flame, thus giving out light. It requires thrice its volume of oxygen or 15 times its volume of air for complete combustion—

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Oxygen.}}{3\ O_2} = \underset{\text{Carbon dioxide.}}{2\ CO_2} + \underset{\text{Water.}}{2\ H_2O.}$$

Hydrogen, the most abundant constituent in coal-gas, merits separate attention, especially as its properties may in many respects be taken as typical of those of inflammable gases.

As its name implies, it is a constituent of water (H_2O), which consists of a compound of hydrogen and oxygen, and from which it may be obtained in several ways, one of the simplest being to take advantage of the strong affinity which certain metals possess for oxygen. With some metals this affinity is so strong that they, by mere contact with water at the ordinary temperature, turn out the hydrogen; thus sodium acts upon water in accordance with the equation—

$$\underset{\text{Sodium.}}{2\ Na} + \underset{\text{Water.}}{2\ H_2O} = \underset{\text{Sodium hydroxide.}}{2\ NaOH} + \underset{\text{Hydrogen.}}{H_2.}$$

The sodium hydroxide (caustic soda) remains in solution in the water and the hydrogen escapes as a gas.

A cheaper way of obtaining hydrogen from water is to use iron instead of sodium. To prepare the gas by this method it is necessary to raise the iron to a red heat and use the water in the form of steam. The reaction is carried out by blowing steam through a red-hot iron tube filled with iron borings or scrap iron; oxide of iron is formed, and hydrogen passes on and may be collected over water—

$$\underset{\text{Iron.}}{3\ Fe} + \underset{\text{Water.}}{4\ H_2O} = \underset{\text{Iron oxide}}{Fe_3O_4} + \underset{\text{Hydrogen.}}{4\ H_2.}$$

Another method of obtaining hydrogen is to treat a metal, *e.g.*, zinc or iron, with diluted sulphuric acid ("oil of vitriol") or hydrochloric acid—

Fe	$+$	H_2SO_4	$=$	$FeSO_4$	$+$	H_2.
Iron.		Sulphuric acid.		Iron sulphate.		Hydrogen.

Fe	$+$	$2\ HCl$	$=$	$FeCl_2$	$+$	H_2.
Iron.		Hydrochloric acid.		Iron chloride.		Hydrogen.

The sulphate or chloride formed remains dissolved in the water present, and the hydrogen escapes as a gas.

Hydrogen when pure is a colourless, tasteless, odourless gas; ordinary specimens have a disagreeable smell, owing to the presence of hydrocarbons and other impurities liberated at the same time as the hydrogen. It is only slightly soluble in water, and is the lightest of all known substances, 1000 cubic feet at 32° F., and 30 inches mercury pressure weigh only 5.59 pounds; the same volume of air under the same conditions weighing 80.5 pounds. In consequence of its lightness, it rises in the air, and was formerly used for inflating balloons, but is now replaced by coal-gas, which, though much heavier (about 7 or 8 times as heavy), is cheaper and more easily obtained; the balloons for coal-gas have to be made considerably larger than those for hydrogen, for the same lifting power.

When heated in contact with air or oxygen, hydrogen takes fire and burns with an almost invisible flame, which, though non-luminous, is intensely hot, producing, by its union with oxygen, water in the state of steam.

The combination of oxygen and hydrogen only takes place when the two gases in contact with each other are raised to a sufficiently high temperature. A jar of hydrogen burns, when a flame is applied, only at its mouth, where it is in contact with air; if the taper be pushed up into the jar not only will the gas fail to burn there, but the taper will be extinguished, since the hydrogen shuts off from the flame of the taper all access of air (Fig. 20).

FIG. 20.—Experiment showing the action of a flame upon Hydrogen.

If hydrogen be mixed with air or oxygen and a flame be applied to any portion of the mixture the union of oxygen and hydrogen begins at the flame, but spreads to all places where oxygen and hydrogen are in contact, *i.e.*, throughout the whole mixture. The flame which is produced by this union spreads with great rapidity, consequently there is a sudden development of heat, and this produces a rapid expansion of the gases themselves and of the product of their union, the steam formed. This sudden expansion drives back the air by exerting great pressure in all directions, and thus gives rise to what is called an *explosion*. Such an explosion is a type of most gaseous explosions, and may occur whenever we have a mixture of two gases whose combination is attended by an evolution of heat. The ordinary laws affecting combustion, however, apply to this case; in order to start combination the temperature of a portion of the mixture must be raised to the ignition point, and it is necessary, if the combustion is to spread, that the heat produced by the union of the gases in one small portion of the mixture should be more than sufficient to raise the temperature of the adjacent gases to their ignition point. Any circumstance which will interfere with the fulfilment of this second condition will prevent the combustion spreading, and so, with such a mixture, though combination might go on near a source of heat, the combustion would not spread throughout the mixture, or, in other words, the mixture would not be explosive. It is obvious, therefore, that if there be present in the mixture

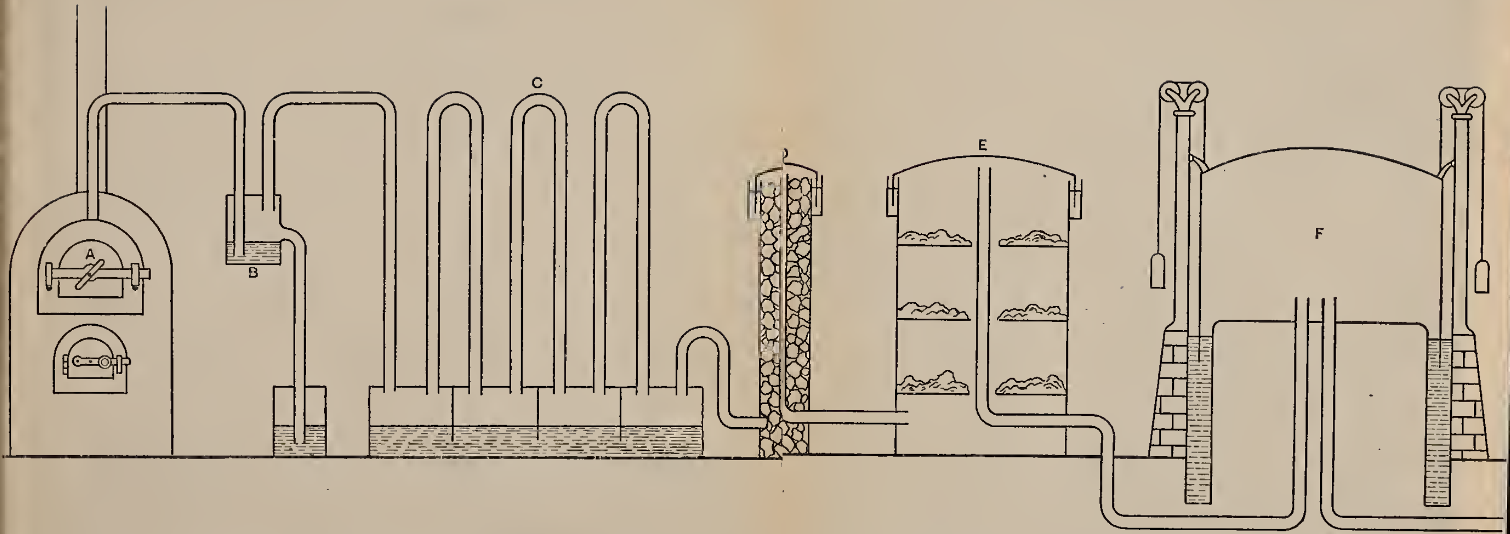

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FIG. 19.—Diagrammatic View of Coal-Gas Plant. A, Retort; B, Hydraulic Main; C, Refrigerators; D, Scrubber; E, Purifier; F, Gas-Holder.

To face page 47.

any gas or gases which do not take part in the reaction, and which, therefore, do not aid in the production of heat, that the conditions are unfavourable to the maintenance of the high temperature necessary for the propagation of the explosion. Such indifferent gas may be a third gas of inert properties, like nitrogen, or it may be excess of either of the gases between which union is to take place. The excess of either gas will plainly be a means of lowering the temperature, since it cannot take part in the production of heat, owing to lack of the other gas with which to combine. Accordingly it is found that mixtures of oxygen and hydrogen, like all mixtures of inflammable gases with oxygen or air, are only explosive when the constituents are present in quantities which are between certain fixed ratios to each other.

The most explosive mixture is, as we should expect, the one containing exactly the ratio of oxygen to hydrogen that occurs in water, viz., 1:2 by volume; there then being no excess of either gas. Any departure from this ratio means an excess of one or other gas, which in either case acts as a diluent, and consequently as a cooling agent to the gases actually combining. If a third gas, indifferent to both those combining, be also present, it is clear that the range of explosibility will be smaller. Thus it is found that explosive mixtures of inflammable gases with air have much smaller ranges of variation in composition than have mixtures of the same gases with oxygen.

(The range of explosibility of various combustible gases with air is given in the table on page 105.)

A substance which will combine with the oxygen of the air with production of heat and light is generally said to be "combustible," while any gas which will allow ordinary "combustibles," *e.g.;* tapers, to burn in it is called a "supporter of combustion." Used in this sense, the terms are fairly satisfactory, and have a definite meaning, but there is a great danger of deducing a totally incorrect idea about the parts played in combustion, by the two substances whose combination brings about the burning. An impression is very frequently conveyed by the use of these terms, that one body "burns" while the other "supports" its combustion, meaning by these expressions that the parts played by the two substances are essentially distinct from each other. A few experiments will show the inaccuracy of these views when held with reference to the combination of two gases. If a jet of hydrogen be lighted and immersed in a jar of oxygen, the hydrogen is said to be burning in oxygen, and the oxygen is said to be supporting the combustion of the hydrogen flame (Fig. 21).

Fig. 21.—Hydrogen burning in Oxygen.

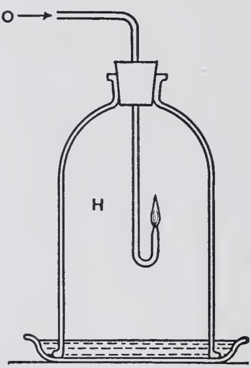

Fig. 22.—Oxygen burning in Hydrogen.

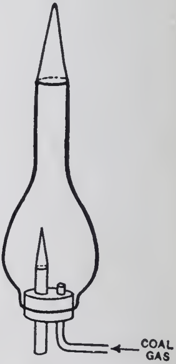

Fig. 23.—Air burning in Coal-gas.

This is true, but these terms only describe the phenomena in so far as it is affected by the circumstances of the case. If a jar of hydrogen be taken and a light be applied to it where the hydrogen is in contact with air, a flame is obtained; if, now, a jet of oxygen be pushed through the flame into the hydrogen, a flame is found to follow the jet, and to all appearances the oxygen burns in the hydrogen and the hydrogen supports the combustion of the oxygen (Fig. 22). What happens is the same in both cases, combination occurs and a flame is produced where the oxygen and hydrogen come in contact, and it is a mere question of circumstance as to which gas appears to burn. The same fact can be illustrated by a still simpler experiment (Fig. 23). Let a glass lamp chimney be fitted with a large cork at its lower end and two tubes be arranged through the cork, one a narrow one, which can be connected with the gas supply by means of an india-rubber tube, and the other a straight, wider tube, just long enough to pass through the cork. Let the lamp glass be supported in a vertical position and the coal-gas turned on; after a few seconds apply a light to the top of the chimney, when the coal-gas will inflame and burn at the top with the ordinary yellow, smoky flame. The draught produced by the coal-gas and flame will cause an inrush of air through the open, wide tube at the bottom of the chimney. If a lighted taper be pushed quickly up this wide tube it will be found possible to ignite the coal-gas and air just where they mingle, *i.e.,* at the top of the wide tube; if, now, the access of air be partially stopped by placing the finger over a portion of the opening at the lower end of the wide tube, it will be possible to regulate the size of the flame at the top of this tube to any desired extent. Here, again, there are two cases of the combination of coal-gas and air going on at the same moment, giving rise to apparently different phenomena. At the top of the chimney there is the usual phenomena of *coal-gas* *burning in air,* while inside the chimney, at the top of the wide tube, through which the air rises, there is *air burning in coal-gas.* It must be distinctly understood that the two phenomena are essentially the same, except in so far as they are governed by circumstances. The term *"combustible"* is applied to whichever gas is delivered gradually into an atmosphere of the other, while the term *"supporter of combustion"* applies to the gas present in larger quantity, therefore encircling the flame, which in all cases is produced only where combination occurs, that is, at the place where the two gases are in contact.

It is thus seen that any gas whose combustion with another is attended by the production of a flame may act either as a "combustible" or as a "supporter of combustion" according to circumstances.

In the case where one of the substances is a solid, it is difficult to arrange that it should act as a "supporter of combustion,"* but it must be remembered that the fact that it always functions as the "combustible" is only due to its being a solid and not to any essentially different chemical part that it plays in the act of combination with the gases.

A combustible solid or liquid may, under certain circumstances, behave something like a gas; if it be finely

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* Certain substances which are not capable of uniting with oxygen, and therefore will not burn in air, are rightly regarded as dangerous by insurance people. Such is the case with compounds which are rich in oxygen, *e.g.*, nitrates, chlorates, peroxides, etc. These substances may act energetically in increasing the fierceness of a conflagration, if they are brought in contact with oxidisable materials like wood, etc. This they do by yielding up their oxygen, wholly or in part, to the oxidisable substance, producing a great amount of heat in the process. Advantage is taken of this in the case of gunpowder. Here are two oxidisable constituents, sulphur and charcoal, intimately mixed with an oxidising substance, potassium nitrate (saltpetre), and the high temperature produced by the explosion is due to the heat of combustion of the sulphur and charcoal. It will be seen that there are two essentially different and opposed classes of substances represented in gunpowder—the oxidisable, carbon and sulphur, and the oxidiser, potassium nitrate. It is obvious that in this case we cannot say which is the "combustible" and which is the "supporter of combustion."

divided and suspended, as a dust in an atmosphere containing the gas with which it can unite, the mixture resembles very closely a mixture of two gases which are ready to combine, and, like such a gaseous mixture, is explosive. Such explosive mixtures are often produced when an inflammable powder, as certain varieties of dry coal dust, the fragments of cotton in rag grinding, the very finely divided portions of flour in a corn-mill, or the spray of an inflammable liquid, becomes suspended in air; and very violent explosions have resulted from the contact of such mixtures with a flame. The violence of dust explosions is increased by the circumstance that in many cases the effect of the explosion of a portion of such a mixture produces so great a disturbance in the air that large quantities of dust lying around are scattered, so the explosion is propagated over a much larger area than might be covered by the explosive mixture at the moment of ignition; the explosion, in fact, acts as a feeder to itself.

One general after effect of such explosions is that the atmosphere left after the explosion in nearly all cases contains *carbon monoxide,* a gas whose poisonous nature is very remarkable. In a coal mine, where the renewal of the atmosphere is necessarily a work of time, the presence of this carbon monoxide after a dust explosion is one of the most important features, for in most cases the fatal effects of such explosions are to be attributed to the *after-damp,* rather than to the explosion itself.

Hydrogen shows, perhaps better than any other gas, the phenomena of *diffusion.* It will be best to approach the study of this subject by the consideration of an experiment which, in addition to introducing the subject of diffusion, serves as an epitome of the properties of hydrogen. Let a bell jar (Fig. 24) be fitted with a cork, through which passes a brass tube provided with a stop-cock. Let the bell jar be filled with hydrogen, the stop-cock being closed. The hydrogen may be confined by allowing the whole to stand in a tray of water. If the jar be removed from the water and the stop-cock opened the hydrogen will escape from the brass tube, its place being taken by the much heavier air which enters at the bottom, and if a light be applied, the jet of hydrogen will burn with an almost invisible flame. It will be noticed that the flame, at first large, will gradually diminish in size, then descend the tube, and finally the contents of the bell jar will detonate sharply. Now, one would have expected that the hydrogen would have been pushed upwards pretty completely by air (which is 14.4 times as heavy) and that it would have burnt quietly at the top of the tube until it was completely used up, and that then the flame would have simply gone out. Evidently, however, a considerable amount of mixing must have occurred in the bell jar between the hydrogen and air despite their great difference in density.

FIG. 24.—Bell Jar of Hydrogen, showing its Inflammability, Lightness, and Diffusibility.

If two flasks be connected together by a long tube passing through holes in the corks which close the flasks, and one flask be previously filled with hydrogen and the other with carbon dioxide (which is 22 times as heavy, bulk for bulk, as the hydrogen), and if the apparatus (Fig. 25) be so arranged that the carbon dioxide is in the lower flask and the hydrogen is in the upper one, and the whole be left undisturbed for an hour or so, it will be found that, contrary to what might have been expected, a considerable quantity of the light hydrogen has found its way into the lower flask, while an equal volume of heavy carbon dioxide has moved into the upper flask.

This mingling of two gases when placed in contact, in spite of their relative heaviness, is known as the diffusion of gases and is explainable on the kinetic theory, which supposes that a gas consists of immense numbers of molecules moving about with great velocity and continually colliding with each other and with the walls of the containing vessel. The mean velocity of the particles of any particular gas increases with a rise of temperature; the pressure exerted by a gas is really due to the blows delivered by the molecules upon any body with which the gas is in contact. A little thought will show that, if the number of molecules in equal volumes of different gases is the same, the two factors upon which the pressure of a gas depends are the weight of each molecule and the average velocity with which those molecules move. To apply to a particular case consider the two gases, oxygen and hydrogen; if they exert the same pressure and if, as there is every reason to believe, equal volumes of the two contain the same number of molecules, then it follows that since the oxygen molecules are about 16 times as heavy as the hydrogen ones they will not have to move so fast in order to produce the same pressure by their impact against the walls of the vessel containing them. It might be thought that the hydrogen particles would have to move 16 times as fast as the oxygen particles in order that their impacts might be equal, and that would be true if we only considered one blow. In consequence of their greater speed, however, the hydrogen particles will strike

FIG. 25.—Apparatus to show Diffusion of Carbon Dioxide and Hydrogen.

the walls of the vessel more frequently than the oxygen ones; in fact, if they moved 16 times as fast as the oxygen particles, they would deliver 16 times as many blows per second on the unit area. The total effect, then, would be that they would deliver 16 times as many blows, each blow being equal to the one delivered by an oxygen particle. It is obvious, therefore, that the mean velocity of the molecules of two gases is not inversely to the densities of the two gases. If, however, it be assumed that the hydrogen move 4 times as fast as the oxygen particles, then they will deliver 4 times as many blows per minute. Here each blow of a hydrogen particle is only one-quarter as violent as those of the oxygen, but there are 4 times as many blows delivered per second; hence the total effect is the same in both cases. So with other gases. it will be found that theoretically with any two gases their particles move *inversely as the square roots of the densities of the gases.* These theoretical results are confirmed by direct experiment. We find in all cases that the molecules of a light gas move more rapidly than those of a heavy gas.

Gaseous diffusion plays a very important part in nature and is one of the greatest agencies tending to bring about uniformity in the composition of the air. It is, therefore, of considerable help in ventilation.

The fact that the molecules of a light gas move more rapidly than those of a heavier one is taken advantage of in Ansell's indicator (Fig. 26) in order to detect the accidental presence in the air of any gas lighter than itself.

The indicator consists essentially of a vessel whose top is formed of a plate of unglazed or "biscuit" earthenware, and whose lower portion is connected with a vertical tube filled with quicksilver. This tube is bent first into a horizontal and then again into a vertical position.

In this second vertical portion of the tube is a rod of metal which nearly touches the quicksilver. The latter is connected with one pole of a battery and the metal rod with the other. Under ordinary conditions, that is, so long as the mercury and the metal rod do not touch each other, no current can pass, and an electric bell placed in the circuit cannot ring. Diffusion takes place through the porous earthenware, but so long as the atmosphere outside consists of gases of the same density as those inside no disturbance of the level of the mercury can occur, for in any given time just as much air enters as leaves the apparatus. If, however, the air outside become impregnated with any gas lighter than itself, then more of that gas will enter the apparatus through the porous diaphragm in a given time than air will leave it, consequently there will be an excess of gas inside. This will exert pressure and force the mercury down in one limb of the tube and up in the other, thus bringing the

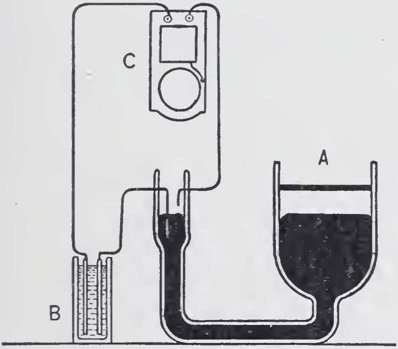

FIG. 26.—Ansell's Indicator. A, the Porous Earthenware Plate; B, Galvanic Battery; C, Electric Bell.

mercury into contact with the metal rod, so completing the circuit and ringing the bell.

This apparatus (which is also made in a form resembling an aneroid barometer), though primarily intended for the recognition of the presence of firedamp in the air of mines, may be also used to indicate the escape of coal-gas or any gas lighter than air.

CHAPTER V.

FUEL.

Chemical Composition of Wood, Charcoal, Peat, Lignite, Coal, Coke—Petroleum—Coal-Gas—Use of Atmospheric Burners —Producer Gas—Water-Gas—Dowson Gas.

FUEL is the name given to any material which, by its oxidation, yields so much heat that it can be conveniently used as a source thereof. Most fuels contain as their principal ingredients carbon and hydrogen; some contain in addition (1) substances which do not contribute to the heating effect, like mineral matters, which are simply left as ash after the combustion, and (2) bodies which not only do not contribute to the burning, but actually lessen by their presence the heating effects produced by the useful ingredients, carbon and hydrogen; this is the case with oxygen. The properties of oxygen and hydrogen in the free state have already been described; it remains to discuss those of *carbon.* This element is very abundant in nature, being an essential constituent of all living beings, both animal and vegetable. In the free state it is met with in three forms perfectly distinct from each other. These are the *diamond,* the purest form of natural carbon, *graphite* or *plumbago,* and *amorphous carbon,* which latter appears in many varieties, as charcoal, etc.

The properties of the *diamond* are not of any great importance, with the exception of its hardness, which is taken advantage of, in order to cut or scratch hard substances, *e.g.*, glass, hard rocks, etc. Its market price is out of all proportion to its intrinsic value, and is largely due to the brilliancy with which it refracts and reflects light, thus giving it a high value for ornamental purposes.

Graphite, a much less rare substance, is really far more valuable to man. Its most important properties are its unalterability at a high temperature and its power of conducting heat and electricity. These properties lead to its use for mixing with clay for the manufacture of crucibles to stand a high temperature, and for making the terminals between which the electric arc passes in electric lighting. It is also used for lubricating purposes, for protecting iron work from the action of damp air, and in the manufacture of pencils.

The third form of carbon, of which *charcoal* may be taken as a type, fortunately much more easily obtained than the others, is by far the most useful. Its properties will be described under wood charcoal.

The three varieties of carbon may be oxidised if heated to a sufficiently high temperature in contact with oxygen, and all form the same quantity of the same product, carbon dioxide.

FUELS may be divided into three classes:

(1) Solid fuels, including wood, charcoal, peat, coal and coke.
(2) Liquid fuels, including petroleum, tar, etc.
(3) Gaseous fuels, including coal-gas, oil-gas, producer gas and water-gas.

The value of a fuel depends mainly upon the quantity of heat generated by the combustion of the unit weight of the fuel, or, in other words, upon its calorific power or heat of combustion. This can be measured by means of a combustion calorimeter (*q. v.*).

WOOD.—The origin of wood is well known. It is often used as a fuel. Its composition varies considerably, according to the nature of the tree, the age of the wood, the time that has elapsed since the wood was cut, and also the conditions under which it has been kept. Its constituents may be divided into three: (1) woody fibre, which consists mainly of cellulose, $C_6H_{10}O_5$; (2) the constituents of the sap, and (3) water.

The last constituent, which is worse than useless as a fuel, is very variable in quantity. In freshly cut wood it varies with the time of cutting, being greater in April than in January. Newly felled sycamore contains 27%; ash, 28%; oak, 35%; while in elm as much as 45%, in fir, 45%, and in larch, 49% are present. Ordinary air-dried wood contains, on a general average, about 20% water, 40% carbon, 4.4% hydrogen, 35% oxygen and nitrogen, and 1% ash.

Wood, when quite dry, is very easily inflamed, and often plays a large part in spreading conflagrations. Its susceptibility to ignition depends very largely upon its composition, and upon the presence or absence of resinous matter.

The ash of wood varies from 1-2%, and is greatest in the younger portions.

Neglecting the ash, the composition of several varieties of dried wood is given in the following table:

	Carbon.	Oxygen.	Hydrogen.	Nitrogen.
Beach	50	43	6	1
Oak	50.6	42	6	1.3
Willow	51.8	41	6.2	1

Charcoal is prepared from wood by the action of heat without access of air. Where wood is plentiful charcoal is made in heaps, the heat necessary for the carbonisation of the main portion of the wood being produced by the combustion of another portion. In England, charcoal is usually prepared by heating wood in retorts, whereby the volatile products, which are destroyed in the former method, are obtained; they, indeed, are often more valuable than the charcoal itself. They comprise "pyroxylic spirit" or wood naphtha (methyl alcohol), acetone (see Chap. XI., page 198), tar, pyroligneous acid (crude acetic acid) and other products.

Charcoal is a black, porous solid, apparently much lighter than water, but really (when the air in its pores is removed) having a sp. gr. of about 1.5. Its more important uses, other than as a fuel, depend upon its porosity, by virtue of which it has the power of absorbing large quantities of gases.

Volume of gas absorbed by one volume of charcoal.

Ammonia	170
Carbon dioxide	68
Oxygen	18
Hydrogen	4

This property is of importance, as it leads to the employment of charcoal as a means of preventing annoyance from the putrefaction of animal matter, and also to its use in making respirators for filtering air containing various noxious gases. Men provided with these respirators are enabled to breathe with impunity an atmosphere which would speedily overpower any one breathing it in the ordinary way. Another use to which charcoal is put, based upon the same property of porosity, is as a decolouriser of organic liquids, like sugar-syrup, etc. The form of charcoal which possesses the power of removing colouring matters from liquids to the highest degree is *bone-black,* obtained by the action of heat upon bones in closed retorts. This substance contains only about 10%

carbon, the remaining 90% being mainly phosphate of lime.

Another important result follows from the porosity of charcoal. When it is freely exposed to air, especially if in a finely divided condition, and fresh from the retort or heap, in which it was carbonised, it begins to absorb and condense in its pores the oxygen, and sometimes this condensation is attended with the production of such a quantity of heat that ignition occurs.

Ordinary black charcoal is somewhat difficult to ignite and to keep burning without a forced draught. A very great difference exists in the relative ease of inflammation of various samples of charcoal. Generally speaking, the higher the temperature at which the wood was charred the higher is the temperature of ignition of the charcoal.

The connection between the temperature of charring and the temperature of ignition of the resulting charcoal is given in the following table:

Temperature of charring.	Ignition temperature.
260-280° C.	340-360° C.
290-350° C.	360-370° C.
430° C.	400° C.
1000-1500° C.	600-800° C.

The charcoal produced by heating wood at low temperatures, say, about 270° C. (518° F.), is brown in colour, ignites readily and contains only about 70-75% carbon, while that obtained by heating to an intensely high temperature, *e.g.*, a white heat, is black, hard, brittle, almost incombustible, and contains 95-97% of carbon.

LAMPBLACK is another form of carbon; it consists essentially of the soot from the very smoky flames produced by burning in a deficient supply of air highly carbonaceous substances, like resin, fats, oils or tar. The soot is condensed often on cloths hung up in chambers through which the smoke has to pass or on the surfaces of revolving metallic cylinders cooled by water. The soot is mainly carbon, but sometimes contains small but important quantities of oil, which have escaped combustion. Such lampblack is very liable to spontaneously ignite when it is first exposed to the air. Lampblack from natural gases in America is called *carbon black,* and is now very much employed. *Drop-black* is charred vine refuse. Lampblack is now sometimes made by detonating acetylene in a closed space, when lampblack and hydrogen are formed.

PEAT consists of the decayed remains of plants growing in swampy places, mixed with earthy and mineral matters. When freshly cut it contains a large amount of moisture. In air-dried specimens the water ranges from 10-25%. Its composition varies, but it generally contains in the dry product:

	Per cent.
Carbon	58-61
Hydrogen	5-7
Oxygen	28-32
Nitrogen	1-2

In addition there is usually from 2-10% ash. Peat is a very bulky substance, and is only used locally as a fuel. It is largely employed as litter in stables, but if pyrites be present, as is often the case, it is not suitable for this purpose, as the pyrites very probably contains small quantities of arsenic, which renders the resulting manure destructive to plant life.

LIGNITE is another product of the decay of vegetable matter in presence of water. It is not often used in England, but is important as a fuel on the continent. It is more carbonaceous and much more compact than peat. Its composition is (in dried specimens):

	Per cent.
Carbon	63-71
Hydrogen	4-6
Oxygen and nitrogen	28-35
Ash	1-14

Air-dried lignite contains about 15-20% water. In Germany lignite is often dried, crushed and then compressed into a compact mass, known as press coal. During the drying and crushing of the lignite, fires and explosions, probably due to dust and possibly helped by inflammable gases evolved from the lignite, often occur. The temperature attained in the drying apparatus seldom exceeds 70° C.

Coal is by far the most important fuel. It consists of the remains of plants which grew ages ago, and which have undergone various fermentative changes, leading to a loss of oxygen and hydrogen and a smaller portion of carbon, thus resulting in a substance much richer in the last-mentioned element than the original vegetable fibre. Its composition varies between very wide limits, as shown in the table of analyses of various coals given on page 46.

The extremes in chemical composition are Welsh anthracite and cannel—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Ash.
Welsh anthracite	90.6	3.6	3.8	0.3	1.7
Boghead cannel	65.7	9.0	4.8	0.7	19.8

Some coals are extremely difficult to ignite, *e.g.*, anthracite, while others are set on fire with great ease, *e.g.*, bituminous coals or cannels. Anthracite, too, when ignited burns almost without flame, but bituminous.

caking coals burn with a long flame, and tend to yield a large amount of smoke. Many coals contain various gases locked up in their pores; these gases escape when the coal is exposed, and issue into the air of the mine, requiring abundant ventilation in order to keep their proportion to air as low as possible.

The gases contained in coal vary greatly in composition, but carbon dioxide and marsh-gas are invariably present, and often small quantities of air, ethylene and carbon monoxide. The two first mentioned are always produced by the decay of vegetable matter beneath water, and their occurrence in coal affords additional evidence of its vegetable origin. These gases are contained in the coal under enormous pressure, sometimes disseminated all through its mass, sometimes accumulated in cavities. From these latter they escape with great violence, when the cavities are broken into, giving rise to an impetuous rush of gas into the mine, known as a "blower." In many cases the gases called by the miners *firedamp,* escape from almost every part of the face of the coal, sometimes with a slight hissing sound; coal evolving its gases in this manner is known as "singing coal."

Outbursts of firedamp into the air of a mine are dangerous occurrences on account of the explosive nature of mixtures of firedamp with air. They are generally influenced greatly by a sudden change in the barometer, not so much that a fall of the barometer is productive of an increased rate of escape of the gases from the coal, for the pressure of these gases is so great, amounting to many atmospheres, that a variation of an inch or two of mercury can make little or no difference to their rapidity of emission, but mainly because in most mines there are portions of the workings which are no longer used, and, therefore, not ventilated. Such cavities often become richly charged with firedamp, as this atmosphere is only renewed by the slow process of diffusion through, perhaps, a very narrow communication with the main galleries. When a fall in the barometer occurs, the pressure of the air in the air-ways is considerably reduced, a large volume of the gases which have accumulated in these old workings, is discharged into the air-ways at a faster rate, perhaps, than the ventilation of the mine can cope with.

Coal which has been raised from a mine and stacked in large heaps continues to lose the gas occluded in it for some time afterwards, and may give rise to the production of an atmosphere explosive or inflammable, as, for instance, in the hold of a ship. This inflammable gas may accidentally become ignited and cause a fire; hence the need of ventilation in the hold of a vessel laden with coal, and the necessity for prohibiting the introduction of a naked light.

The ash of coal varies in amount from 1% to as high as 30% or 40%, but a good coal should not contain more than 5% or 6%. The sulphur in coal also varies between wide limits, from .4% to 2% or 2½%, and apparently exists in two states of combination—in the organic portion of the coal and as iron pyrites; also sometimes as sulphates. The pyrites is of considerable importance, since upon its presence and amount the liability to spontaneous ignition which some coals show so largely depends.

Iron pyrites is a mineral composed of iron and sulphur in the proportion shown in the formula FeS_2. It exists in two modifications, both of which occur as "coal brasses." One, known as *"yellow pyrites"* or *"mundic"* crystallises in the regular system, and is not very easily oxidisable; the other, known as *"white pyrites"* or *"marcasite,"* crystallises in the rhombic system, and is much more prone to oxidation, especially in a damp atmosphere.

When oxidation occurs there are formed sulphate of iron and sulphuric acid in accordance with the equation—

$$\underset{\text{Pyrites.}}{FeS_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Oxygen.}}{7\,O} = \underset{\text{Iron sulphate.}}{FeSO_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$

This process, like all oxidation processes, generates heat, and if this heat be not carried away by a stream of air, the temperature rises, oxidation proceeds more and more rapidly, until finally the temperature of ignition of the coal is reached, and the mass bursts into flame. In this way fire sometimes breaks out where a large amount of coal is stored and no adequate ventilation is afforded. The presence of large amounts of pyrites, especially marcasite, is, therefore, a source of danger, as well as objectionable in other ways; all sulphur in coal is harmful, since when the coal is burnt a large portion of the sulphur is converted into sulphur dioxide, which escapes into the air, eventually produces sulphuric acid, and acts injuriously upon articles of the household, especially leather, and on surrounding plant life. The gases evolved by the burning of coal containing sulphur, too, act corrosively upon the iron in the fire bars, etc.

Some cases of spontaneous combustion in coal have occurred when the blame could not be attributed to pyrites. Coals practically free from this substance have undergone spontaneous ignition. In these cases the cause has been assigned to the power which some coals have of absorbing and condensing in their pores the gases of the air, thus producing heat and ignition, after the manner of charcoal, already referred to. The organic matter, too, seems to suffer oxidation, especially when warmed and exposed to air, and this change aids in bringing about spontaneous combustion. It is to be noted in this connection that while the oxidation of pyrites is favoured by moisture, the absorption of oxygen, etc., by porous coal is rather hindered than encouraged by the presence of water.

In both cases the danger is lessened by *good* ventilation, which ensures that the heat shall be carried away as fast as it forms, so that the temperature never rises dangerously. Unless, however, the ventilation be very good, no ventilation at all is better, as limited access of air is often found to be favourable to spontaneous combustion. (See also Chap. XIV.)

Coke is coal which has been heated so as to drive off all substances which are volatile. It consists mainly of carbon, but retains all the ash of the coal and small quantities of hydrogen, oxygen, nitrogen and sulphur. It is sometimes made, for use in metallurgical operations, like iron smelting, by special coke ovens, where the coal is heated out of contact with air, while another variety of coke results as a by-product from the manufacture of coal-gas. The two products differ mainly in physical structure. The amount of coke yielded by coal varies from 55% or 60% to as high as 90%; it is usually 65-70% of the weight of the coal.

Coke contains 85-90% carbon, .5-1% hydrogen, 1-2% oxygen, 1% sulphur, 2-20% ash (usually about 4% or 5%).

Coke is very difficult to ignite, and can only be kept burning by a good draught of air.

Petroleum is the best example of a liquid fuel. It is only used on a large scale in the neighbourhood of the petroleum wells, *i.e.*, in Russia, near Baku, and in Pennsylvania. "Astatki" or "Massud," as the residues left after the distillation of the burning and lubricating oils are called, is largely used as fuel for locomotive and marine engines. It is burnt either by sending it into the furnace as spray by means of a jet of air or steam (Figs. 27 and 28), or by means of Nobels' troughs.

"Astatki" contains usually 84-85% carbon, 13% hydrogen, 2% oxygen.

Sometimes petroleum oil is used, as in oil engines, for preparing an explosive mixture with air; such a mixture can be obtained in two ways: (1) By using a very volatile oil, say "gasoline" or "rhigolene," which will volatilise at about the ordinary temperatures, or by heating ordinary kerosene oil in a vapourising chamber; or, (2) Introducing air containing fine spray of petroleum into the cylinder and exploding the mixture. Another use of petroleum, especially of the volatile portions, *e.g.*, "benzoline," is in the lamps which burn with a non-luminous flame, used by painters, plumbers, etc. These lamps are generally constructed in such a way that the liquid fuel is forced by pressure (either by compressed air pumped into the liquid receptacle by hand or, more generally, by the vapour pressure of the liquid itself; this pressure, greater than atmospheric, being exerted because of the receiver becoming warm by conduction of heat from the flame) into a metal chamber, where it is volatilised, and issues as vapour through a small hole; the jet of vapour draws in air through holes made for the purpose, and the mixture of vapour and air then burns, generally from an opening covered with wire gauze. In order to start such lamps, it is necessary to heat the burner and the volatilising chamber by means of a flame, usually that of a little methylated spirit poured into a small cup fitted for the purpose. The apparatus works well in practice, but there

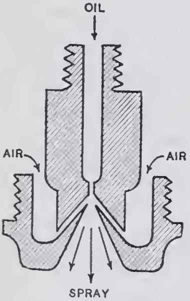

FIG. 27.—Oil Sprayer (Compressed Air).

is a possible danger of the pressure inside becoming sufficiently high to burst the vessel, when a serious accident would probably ensue.

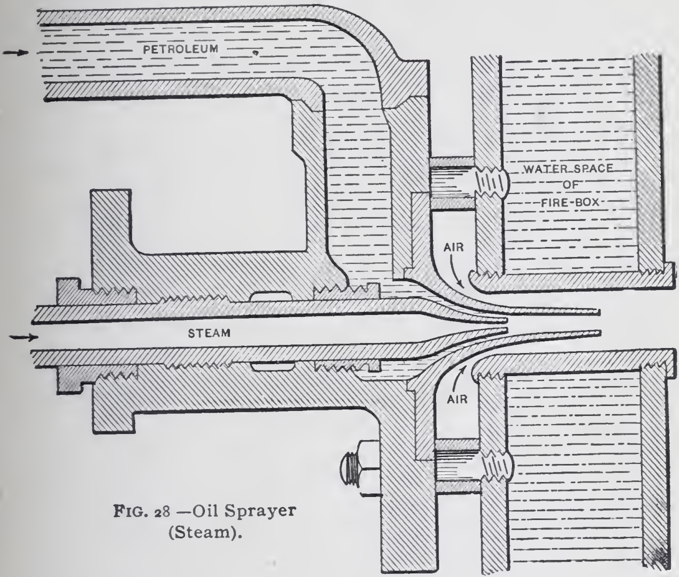

FIG. 28—Oil Sprayer (Steam).

COAL-GAS.—A brief description of the method of preparation of this substance has already been given (see page 46). Though generally regarded as an illuminant, coal-gas is becoming more and more used as a fuel. When burnt in the ordinary way, *i.e.,* as it issues from an orifice into the air, it yields a smoky, luminous flame, depositing soot upon any solid object with which it comes in contact. This action is objectionable in many ways, perhaps the greatest drawback being the waste of heat consequent upon the bad conductivity of a layer of soot. The deposition is an evidence of the presence of solid particles in the flame, and since these solid particles of carbon are the main factor of conferring luminosity, it may be well to consider here the general structure of a luminous flame.

An ordinary coal-gas flame consists of three distinctly marked areas. In the centre are the unburnt gases coming from the burner, these are surrounded by a sheath of a bright yellow colour, the region of the flame which gives the main portion of the light, and, lastly, surrounding this is another sheath, which is almost invisible, but intensely hot.

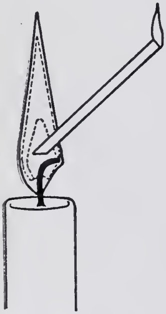
FIG. 29.—Structure of Candle Flame.

Since ordinary gas flames are of such a shape as to render it difficult to see distinctly the three areas just described, it is better to study a candle flame, in which the parts are much more clearly defined, and whose shape is not modified by artificial means, as is that of a gas flame. The similarity between a candle and coal-gas flame is very close; in fact, a candle flame is practically a gas flame, for a candle may be said to be a small gas-making machine which burns its gas as fast as it is made. Surrounding the wick of the candle is a dark area, easily seen, consisting of the gases evolved from the wick. Their existence in this portion may be demonstrated by the introduction of a short piece of glass tubing held in an inclined position in the flame (Fig. 29). The gases are thus extracted, and may be lighted at the other end of the tube.

Surrounding the dark central space is a large brightly luminous portion, from which the light emanates. In this region there are large quantities of solid particles of carbon, as can be proved by the introduction of any solid substance into the flame, when an immediate deposit of soot, which is almost pure carbon, is obtained.

The separation of carbon in flames has been ascribed to various causes. An explanation often given some years ago, was to the effect that to this portion of the flame oxygen could penetrate only to a limited extent, and there was thus a struggle between the constituents of the coal-gas for this oxygen; that the hydrogen having the stronger affinity left the carbon with which it had been combined to unite with the oxygen to form water, the carbon thus separated from the hydrogen and not having oxygen to combine with in this region, formed into solid particles, and these, being intensely heated, gave out light until, on coming out further from the central portion of the flame, they met with oxygen of the air and were eventually oxidised to carbon dioxide. This explanation, though very plausible, has been proved to be untrue, for it has been conclusively shown that when there is a struggle for oxygen between carbon and hydrogen the carbon gets the oxygen, forming therewith carbon monoxide, and the hydrogen is left uncombined.

The true explanation is believed to be that the separation of carbon is due merely to the heating effect of the outermost region of the flame upon the hydrocarbons in the gases at the centre. It is well known that heavy hydrocarbons, when raised to a high temperature, without contact with oxygen, decompose, separating carbon and forming hydrocarbons of simpler composition like marsh-gas.* According to Lewes, acetylene is always formed in hydrocarbon flames, and plays an important part in the production of luminosity. This separation of carbon occurs in the manufacture of coal-gas, where the gas retorts become coated on the inside with a dense deposit of carbon resembling graphite, resulting from the

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* See papers by Lewes and by Smithells in the *Journal of the Chemical Society*, 1892, 1895, 1896.

baking action of the hot walls of the retort upon the hydrocarbons distilled from the coal.

The outer region, which constitutes the third portion, and to which reference has just been made, is almost invisible under ordinary circumstances, but may be rendered evident by several methods. One of the simplest is to hold a match-head, which has been struck and extinguished, near, but apparently not quite touching the flame, when it will be noticed that the flame really extends further outwards than was thought, and becomes coloured violet, owing to the potassium compounds present in the match-head.*

It is obvious that, if the above explanation of the separation of carbon in a luminous gas flame be true, the introduction of oxygen or air into the interior of a flame will prevent the separation of solid particles by oxidising the carbon as it leaves the hydrogen with which it is combined. So, too, we should expect that if we mixed with the gas any indifferent gas like nitrogen that this, by cooling the flame (making it larger), would also interfere with the separation of carbon.

Both these effects are found to take place, and are employed when coal-gas is required for merely heating purposes. Coal-gas is mixed with a certain quantity of air before it is ignited, when it is found to burn without any separation of carbon, and with scarcely any light emission. This method of burning coal-gas was first devised by Bunsen, and the burner he devised and which still bears

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* In this region the carbon is in all flames, burning from properly constructed burners completely oxidised. The blackening effect of gas flames, lamps, etc., upon ceilings and walls is erroneously attributed to soot which they are supposed to emit. The blackening is, in nearly all cases, due to the uprush of hot gases hurling the dust particles, always present in the air, against the ceilings, etc., to which they cling. A similar darkening takes place over a steam or hot-water pipe.

his name may be regarded as the parent form of the many so-called *atmospheric burners.*

Such burners effect the admixture of the coal-gas with the proper quantity of air by virtue of a curious property possessed by a jet of compressed gas when it issues into the air. If the gas escapes from a narrow orifice, it has considerable velocity, and the jet by friction carries with it a certain quantity of air, the place previously occupied by this air being taken by fresh portions which are drawn in. There is thus produced an area of low pressure and a consequent motion of the surrounding air towards the jet itself. It is in this way that all atmospheric burners produce the requisite mixture of coal-gas and air. If the orifice from which the gas issues be enlarged or made irregular, this aspirating effect is interfered with, and the flame then becomes partially luminous. The amount of air which thus mixes with the coal-gas has to be carefully regulated by adjustment of the size of the opening or openings through which the air enters.

If an apparatus were so arranged that coal-gas could burn from the end of a tube and air were added in gradually increasing quantities to the coal-gas before it issued from the tube, the following series of phenomena might be observed. At first, when no air was admitted, the coal-gas would burn with a luminous flame of considerable size and of a very flickering character, easily blown about by a slight draught. As the air was gradually admitted the flame would grow less and less luminous and smaller and smaller in size; then the last portions of luminosity would disappear and the flame would become still smaller and steadier, its colour would be blue or lavender; next an inner cone of green would appear and gradually become more and more clearly defined, the flame at the same time getting smaller and "keener" looking. Finally, if the air were still further increased the inner green cone would descend the tube to the place where the air and coal-gas first come in contact. In some cases the outer part of the flame would be left at the top of the tube as a pale, feeble, cool flame of very flickering character.

The explanation of the above phenomena is as follows: At first the coal-gas burns as usual at the top of the tube, where it is surrounded with air and the luminosity is produced, as already described, by the "baking" action of the outer sheath of gases undergoing combustion upon the heavy hydrocarbons in the coal-gas. As the quantity of air mingled with the gas increases, the separation of the carbon particles becomes interfered with, partly, perhaps mainly, because the oxygen converts them into carbon monoxide, and partly because the inert nitrogen of the air prevents the temperature of the hydrocarbons being raised quite so high as before. As the quantity of air further increases the separation of carbon particles is entirely prevented and the flame becomes perfectly non-luminous, the shrinking in size being due to the fact that the coal-gas is now able to meet with sufficient air for its combustion without spreading itself over so large an area. The appearance of the inner green cone is an indication that the mixture is approaching the point when it is capable of inflammation throughout its mass without the aid of additional oxygen from the outside. In fact, it really means that combination between the two, coal-gas and air, can take place with the production of a flame, but only where the temperature is high, owing to the proximity of the outer flame, in which the substances left after the occurrence of the green flame (being still rich in combustible gases), burn by union with an additional quantity of air from the outside.

As the air in the mixture is further increased, the inner green cone becomes more and more independent of the help of the heat from the outer flame, until a point is reached when the flame could spread throughout the whole mixture. This, however, is not the exact point at which the flame descends the tube. For this descent it is necessary to have more air than is required for the explosibility of the mixture, because the velocity of inflammation of a gaseous mixture varies with its composition and, at the point under discussion, would be extremely small; still if the whole mixture were at rest, *e.g.*, in a jar or bottle, the flame would travel through it. Under the circumstances of the experiment, the flame would not descend unless the velocity of inflammation were greater than the velocity of motion of the gases in the tube. As the air supply increases, the velocity of inflammation increases until finally it becomes greater than that of the gases in the tube. The green cone then descends, the products formed by it pass along the tube until they issue into the air, and, since they contain hydrogen and carbon monoxide, but no free oxygen, they may there burn.*

This series of phenomena has been described and explained at some length because of the frequency of its occurrence, accidentally, perhaps, with atmospheric burners. It is manifest from the above account that if an excess of air enter an atmospheric burner there is great tendency for the flame to "strike back" and burn where the air and gas first touch each other, and since in many cases this is near the place where the burner is attached by a temporary india-rubber tube to the gas supply, there is considerable danger of the heat produced by the flame upon the burner being conducted to the india-rubber, melting it, and so causing an escape of gas close to the burner. The gas may take fire and burn from the end of the rubber

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* See Smithells and Ingle *Jl. of Chem. Soc.*, 1892, p. 204.

tube, this melts and burns away, and so the gas flame retreats along the tube, consuming it as it goes and, in all probability, setting fire to other articles in its neighbourhood. This is a danger attending the use of all atmospheric burners, and is best avoided by the abolition of inflammable substances, like rubber, for the connections; whenever possible metal tubing should, therefore, be employed. In many cases the retreat of the flame along the burner tube, when the air supply becomes excessive, can be prevented by the adoption of wire gauze at the top of the burner. This acts as in the "Davy" lamp (see Chap. I.), enabling coal-gas to be burnt with the admixture of a much larger quantity of air than could possibly be used in a burner without gauze, and thus a hotter (because smaller, with the same amount of gas) flame can be obtained. Such a device is generally employed in the modified Bunsen burners used in *incandescent gas lighting*.

In this system of lighting coal-gas is used simply as a fuel, being burnt in such a way that its richness or otherwise in illuminating ingredients is almost a matter of indifference. The light is obtained by the heating effect of the gas upon a "mantle" made by saturating a cotton fabric, woven to the form desired, with solutions of salts of thoria and ceria, two so-called "rare earths," that is, two oxides of rare metals, thorium and cerium.

The network, saturated with these salts, is strongly heated, whereby the cotton is burnt and completely destroyed (expelled as carbon dioxide and water vapour), leaving a very light, porous mass, retaining the shape of the original mantle and consisting of a mixture of a large proportion of thoria with a little (2%) of ceria. This mantle is rendered more durable for transport by covering it with collodion, which burns off when the mantle is first used. In action the mantle is raised to a high temperature by what is practically a Bunsen flame, except that a larger proportion of air is introduced than could be done in an ordinary way, this being rendered possible by the wire gauze, in the manner already explained.

One of the great objections to the incandescent burner is the fragility of the mantle, so easily shattered by very slight shocks. An attempt to lessen the effect of these shocks by suspending the mantle and burner from above by a spring, attaching it to the gas supply and tap by means of india-rubber tubing, would probably prolong the life of the mantle, but to this method is the great objection to be urged against all atmospheric burners when connected by india-rubber tubes—the danger of the flame "striking back," which may occur in spite of the wire gauze, and setting fire to the rubber and perhaps other bodies—in the manner described. It is no uncommon sight to see street lamps, where this method of lighting is employed, with their burners utterly deranged and the gas burning with an irregular flame from the top of the main, owing to the rubber tube having been thus completely burnt away. In such cases little additional damage is likely to ensue, but the same could not be said if a similar occurrence took place in a house.

A method of suspending incandescent burners and mantles so as to shield them from shocks has just been devised (Clay's patent). In this arrangement the gas-pipe itself is coiled and forms the support and spring whereby the use of india-rubber connections is entirely avoided. The inertia of the burner is increased by fastening a weight to it, so that it can never get up any large amount of vibration, however numerous or severe the shocks may be.

PRODUCER GAS.—This substance is largely employed in many metallurgical and other operations where a high and uniform temperature is required. It is made by passing air over heated coal or coke; the process, once started, maintains itself, as a large amount of heat is produced in the reaction. The main change results in the formation of carbon monoxide by the union of the carbon of the coal or coke with the oxygen of the air.

This reaction may take place in two stages—

$$(1)\qquad \underset{\text{Carbon.}}{C} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Carbon dioxide.}}{CO_2}.$$

$$(2)\qquad \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Carbon.}}{C} = \underset{\text{Carbon monoxide.}}{2\,CO}.$$

In addition to this the water present in the air undergoes decomposition—

$$\underset{\text{Water.}}{H_2O} + \underset{\text{Carbon.}}{C} = \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{CO} + \underset{\text{Hydrogen.}}{H_2}$$

Also if coal be used, as it generally is, some of the hydrocarbons produced by heat from coal are found in the gas, and there is always a small amount of carbon dioxide present. It is to be remembered, too, that the nitrogen of the air passes through the generator unchanged.

The admixture of the air with steam before it enters the apparatus is found to have many useful effects, and is almost always practised. The action of water vapour upon carbon is attended with the absorption of heat; this prevents the too rapid destruction of the fire bars and fireclay lining of the generator, which would occur if dry air were used. Then, too, the gas obtained is enriched by the fact that the portion produced by this action is not necessarily diluted by the useless nitrogen, as is the case with the carbon monoxide formed from the air and carbon. The necessary moisture is derived from a jet of steam used to force the air into the apparatus (Fig. 30), or sometimes the ashes which accumulate under the grate are sprinkled with water.

The composition of the gases produced by a Siemens' generator is shown below:

	Per cent.
Nitrogen	63
Carbon monoxide	23
Hydrogen	3
Carbon dioxide	5
Marsh-gas	6

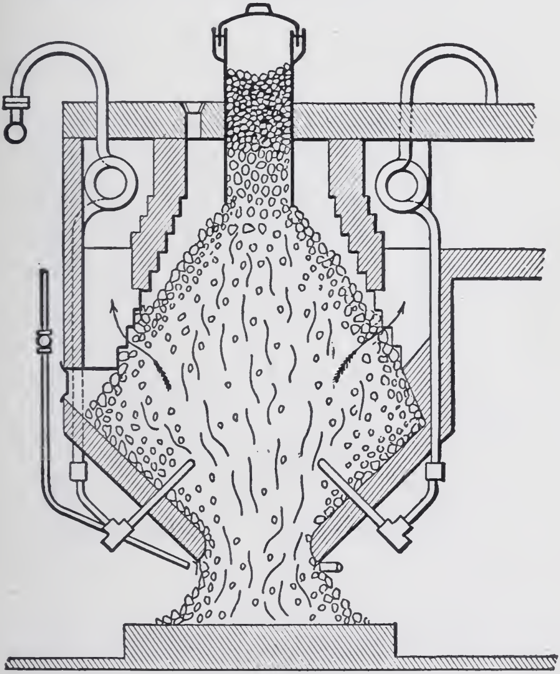

FIG. 30.—Siemens' Circular Gas Producer.

This gas burns in air producing a non-luminous flame, due to the oxidation of the hydrogen to water, the carbon monoxide to carbon dioxide and the marsh-gas to water and carbon dioxide.

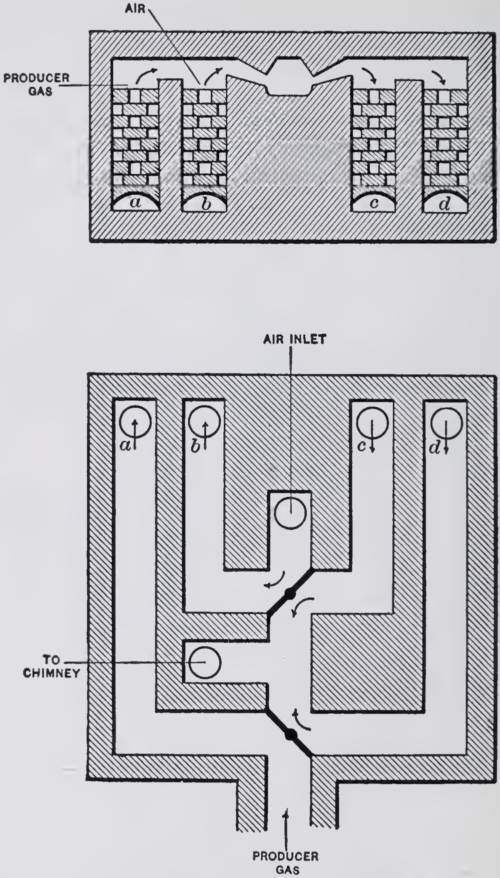

FIG. 31.—Vertical Sections and Plan (of the Flues) of a Siemens Regenerator Furnace.

The great advantage of using producer gas instead of coal or coke lies in the greater control over the temperature it permits, and also in the possibility of using what is known as the "regenerative" principle introduced by Siemens (Fig. 31). This consists in the utilisation of the heat carried away in the products of combustion. The hot gases are led through two chambers lined with fire-brick, filled with tiles also made of fire-brick and arranged in a honeycomb-like manner, whereby the heat from the hot waste gases is absorbed before they, when thus somewhat cooled, are drawn off to the chimney.

The direction of the gases is then reversed, so that the producer gas has to traverse one of these hot chambers before it reaches the furnace, while the air with which it is to combine has to traverse the other one. Both gases are, therefore, raised to a high temperature before they come in contact, so that the heat of their combustion is thus added to the heat they already contain, resulting in the production of a very high temperature. The hot waste gases are in the meantime traversing another set of chambers and raising the temperature of the fire-bricks contained therein. The current of gases is again reversed and so on.

In this way an enormous economy of fuel is brought about and a higher temperature can be obtained. This principle cannot be so well applied when the fuel used is solid, as then it is only feasible to heat the air before combustion and not the fuel also.

Water-Gas.—This product, which has been in use to a small extent since 1823, has in recent years obtained considerable notoriety. In England a good deal of prejudice has existed against this gas from the poisonous effects which it possesses and which have been somewhat strikingly exhibited on several occasions. In this respect it resembles producer gas or even coal-gas, both of which contain the same poisonous ingredient—carbon monoxide—though in a less proportion.

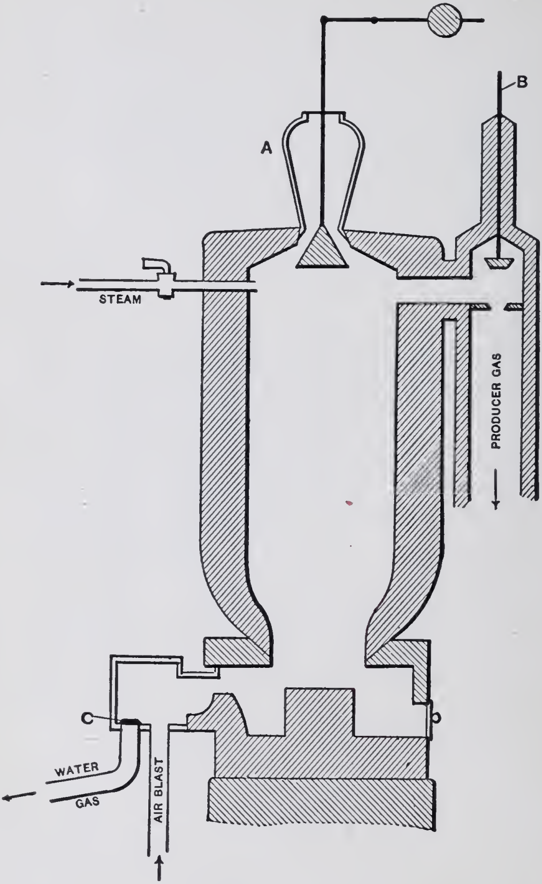

FIG. 32.—Water-Gas Generator. A, Hopper through which Anthracite or Coke is fed; B and C, Valves. The diagram represents the arrangement during the "Hot Blow." For the "Cold Blow," B is closed and C is placed over the Air-Blast Pipe.

Water-gas is obtained by a reaction already referred to, viz., by the action of steam upon carbon—

$$\underset{\text{Water.}}{H_2O} + \underset{\text{Carbon.}}{C} = \underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Hydrogen.}}{H_2}.$$

The gas, however, instead of consisting, as the above equation indicates, of 50% carbon monoxide and 50% hydrogen, always contains some carbon dioxide and generally some nitrogen and marsh-gas.

The reaction represented above only takes place when the carbon is at a high temperature, as the process involves the absorption of a large amount of heat; it can, therefore, only be carried out by the aid of additional heat. In practice this is usually supplied by blowing air through the mass of coke in a suitable furnace, thereby forming "generator gas" or "producer gas" and raising the temperature of the coke and the furnace to a white heat. The air is passed upwards through the mass, the generator gas is led out at the top and utilised elsewhere. This is sometimes called the "hot blow" (Fig. 32), and usually lasts about 10 minutes; next, steam is blown in at the top of the furnace and led downwards through the intensely heated mass, becoming converted into water-gas, which is led away at the bottom, sometimes through a "scrubber," to the gas-holder. The "cold blowing," as it is called, lasts about 4 or 5 minutes, when the temperature of the coke is so lowered that it is necessary to have recourse again to "hot blowing," and the consequent formation of generator gas. By this process about three times as much producer gas as water-gas is formed.

Water-gas usually contains—

	Per cent.
Hydrogen	49
Carbon monoxide	44
Carbon dioxide	3
Nitrogen	4

It is free from dense hydrocarbons, therefore possesses no illuminating power, and is only of value as a fuel. In order to render it suitable for illuminating purposes it is often "carburetted" by mixing it with the vapours of petroleum naphtha and passing the mixture through a hot chamber, where the vapours are decomposed with the production of heavy hydrocarbons.

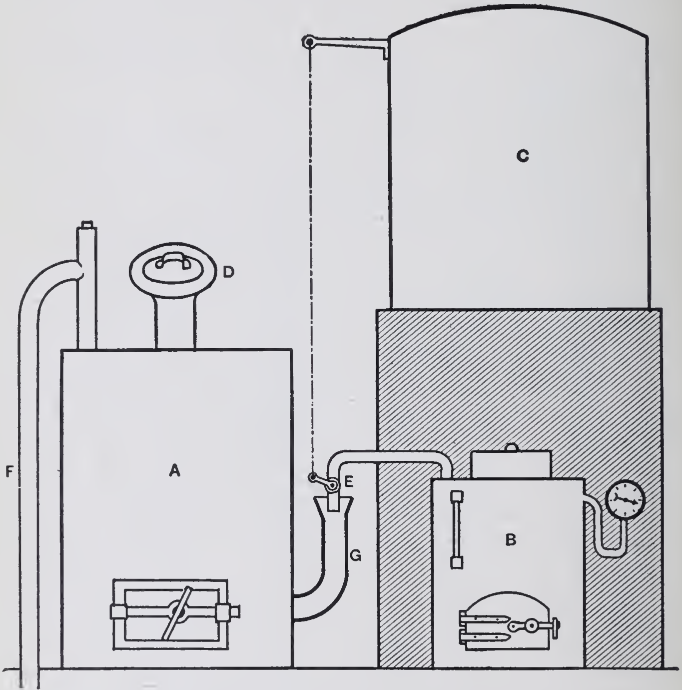

FIG. 33.—Dowson Gas Plant. A, the Generator; B, the Steam Boiler; C, the Gas-Holder; D, the Hopper through which the fuel is fed; E, Steam Jet injecting air through the tube G; F, the Pipe conveying the gas to the Holder C.

It can, of course, be used for incandescent lighting without any necessity for carburetting it. As it is almost perfectly odourless there is a danger of an escape of water-gas occurring without any indication by which it could be detected until its poisonous effects had been produced. This drawback can be got over by adding to it a small quantity of some strong-smelling gas or vapour.

DOWSON GAS.—This is essentially a mixture of producer and water gases, made by blowing steam and air through a funace containing coal. The gas-holder, which serves to compensate for irregularities in production and consumption, is sometimes so arranged that when it rises to a certain point it begins to close the steam cock and thus to diminish the rate of production (Fig. 33). The gas is passed through a "scrubber" and collected in a gas-holder. Its average composition is as follows:

	Per cent.
Hydrogen	17
Carbon monoxide	24
Marsh-gas	1
Carbon dioxide	6
Nitrogen	52

The gases described are used largely as fuel, both in furnaces and in gas engines; it may be of interest to give a table showing the comparative heating effects—

Approximate Calorific Value of 1 Cubic Foot of Gas.

	British Thermal units.
Producer gas	110
Dowson gas	145
Water-gas	290
Coal-gas	670
Acetylene	1,300

(See Chap. VI.)

CHAPTER VI.

ILLUMINANTS.

Candles; Oil, Petroleum, Benzoline and Naphtha Lamps, Coal-Gas, Oil-Gas, Acetylene—Electric Lighting.

Candles.—The old tallow candle is now almost extinct, except for use in mines, etc., where the objectionable smell and dropping of tallow are not of much consequence. Such candles are made by dipping a bundle of cotton threads (twisted, not plaited) into molten tallow, withdrawing it and allowing the fat to solidify, and repeating the process until the requisite thickness is attained. They burn with a flame which emits smoke unless the wick be well attended to—"snuffed." When the flame is blown out the wick continues to smoulder, and emits a nauseous odour, due to the destructive distillation of the glycerine contained in tallow, as in all true fats.

In other modern candles the wick is made much thinner and is plaited, so as to always have a tendency to bend over when released from the candle; the wick, therefore, pushes its free end through the side of the flame, where the air can oxidise it, and so is consumed at the same rate as the candle itself, no snuffing being required.

The materials of which such candles are made may be beeswax, cocoanut oil, paraffine wax, spermaceti, stearic or palmitic acid or ozokerite, or mixtures of these substances. In these cases the wick is held stretched along a mould into which the molten substance is poured and allowed to cool rapidly, often by surrounding the mould with cold water.

Oil lamps, *i.e.*, lamps intended to burn colza, sperm or other true fatty oil, also are almost obsolete for general illuminating purposes, but they are still used as signal lamps on the railway, watchmen's lanterns, etc. They resemble candles in their action, and are liable only to the same drawbacks and dangers.

Petroleum lamps differ from the above class in the greater mobility and inflammability of the substance burnt. The former property of petroleum enables it to rise to a greater height in a wick than a viscid oil could do. Its volatility causes it to emit a vapour which forms an explosive mixture with air; hence petroleum lamps are more liable to accident than colza or sperm lamps. The temperature at which petroleum (kerosene) gives off sufficient vapour to form with air a mixture that will fire by contact with a flame is called its "flash-point" and varies in different specimens, its lowest limit by law is fixed at 73° F. (See Chap. IX.)

The oil reservoirs of a lamp should be of metal, not of glass or porcelain, and the burner so placed that the reservoir does not get hot; should this happen, the oil may be raised above its flash-point and emit enough vapour to yield an explosive mixture with the air above it. Ignition at the flame might then ensue, with the production of an explosion. This explosion, though not in itself very violent (unless the oil vessel be large and nearly empty), is dangerous, since the shattering of the reservoir, which usually happens, scatters and probably ignites the oil.

Lamps are now being made to burn petroleum with a non-luminous flame intended for heating purposes, also for rendering incandescent the "Auer" or "Welsbach" mantles.

The Petroleum Lamp Trades Association of the United Kingdom has recently made the following suggestions to the Petroleum Commission, and these have been accepted—

(1) That the legal flashing point of petroleum oil be altered from 73° to 100° F.* (closed test). Samples having a lower flashing point than 100° F. to be classed and sold only as *petroleum spirit.*

(2) That fragile glass reservoirs should be prohibited, but that glass reservoirs of sufficient thickness be allowed, say, about 1 pound of glass to each pint of capacity.

(3) That the base of a lamp be larger than the diameter of the reservoir and bear in weight a reasonable proportion to the height of the lamp.

(4) That attention should be drawn to the frequently occurring accidents through the use of too small a wick in a burner. That all burners be marked with the size of wick required and that the wicks be sold in lengths with the size marked upon each.

(5) That all burners should have properly constructed wick cases and be attached by a screw collar, not by a plug or bayonet collar, to the reservoir.

(6) That it is very important that there should be greater uniformity in size of wick tubes, collars and screws.

Benzoline lamps in which the volatile portions, "benzine," "ligroine," etc., of petroleum or paraffine are burnt from a wick fed by a sponge soaked in the liquid, have almost fallen into disuse, and rightly so, for they are dangerous in many ways. The liquid is very volatile and gives off an inflammable vapour at the ordinary temperature.

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* See page 167.

Naphtha lamps are chiefly used out of doors. A lamp consists of a reservoir of the liquid, either petroleum spirit or coal-tar naphtha, connected by a tube passing out downwards at its base to a burner consisting of an iron cup with the pipe entering at its bottom and having a kind of iron cage above it. The flow of liquid is regulated by a tap. The naphtha blazes fiercely when ignited and heats the iron of the burner, this vaporises the naphtha as it runs down, giving a vigorous flame not easily extinguished in a wind. The use of such a volatile and inflammable liquid is obviously attended with considerable risks.

Tar, or, more generally, "dead oil" from the distillation of coal-tar, is sometimes burnt for illuminating purposes in an apparatus similar in action to that described as being used in painters' and plumbers' lamps for burning petroleum or benzoline with a smokeless flame. In this case, however, the quantity of air mixed with the vapour from the tar is not sufficient to yield a non-luminous flame. The flame, indeed, is of an intensely bright character, and is often used for illuminating engineering operations in the open air.

Coal-gas has already been described in some detail (see Chap. IV). It remains, however, to say a few words as to its employment as an illuminant.

The cause of luminosity has already been explained; it is to be attributed to the separation of solid particles of carbon and the raising of these to a white heat by the combustion of the gases at the outer part of the flame.

In a coal-gas flame the hydrogen and marsh-gas present, by virtue of their low density, probably diffuse outwards from the centre of the flame more rapidly than the heavy hydrocarbons, *e.g.*, ethylene. Hence the gases in the interior are left richer in these hydrocarbons than the original gas, and the amount of carbon separated is probably increased.

The burners used for coal-gas are of various forms, the commoner being—

(1) The slit or batswing burner.
(2) The union, fish-tail or Manchester burner.
(3) The Argand burner.

These forms are well known and need not be described here.

Attempts were made by Siemens to increase the illuminating power of coal-gas by applying the regenerative principle, already described under Producer Gas. (See Chap. V.) The higher temperature was obtained by causing the products of combustion to give up their heat to the air used to feed the flame. In this way, in the Siemens regenerative burner and also in the well-known "Wenham" burner, a great increase in the amount of light obtainable from a given volume of coal-gas was produced.

A still greater economy of gas results from the use of the "Welsbach" or "Auer" incandescent burner, which has already been described (see Chap. V.), but to explain the increased amount of light emitted is not easy. According to H. Bunte (*Ber. der Deut. Chem. Gesellschaft, 1898,* p. 1), the cause of the high temperature of a Welsbach mantle when heated in a Bunsen flame is to be attributed to the power which ceria possesses, of bringing about more rapid combination between hydrogen and oxygen, consequently producing a higher temperature in the flame. Ceria constitutes about 1% or at the most 2% of the material of the mantle, the main mass consisting of thoria, which apparently does not possess this power. The thoria simply serves as a non-conducting support for the particles of ceria, which are thus prevented from losing their heat except by radiation.

OIL-GAS.—A gas rich in illuminating constituents, is produced by the distillation of oil. The oil often employed is the so-called "solar oil," a product from Russian petroleum, or oils of sp. gr. about 0.84, from shale or American petroleum, oils which are too volatile for lubricating and not volatile enough for burning purposes. They are distilled in hot retorts sometimes, as in the Pintsch plant, by allowing the oil to run into shallow

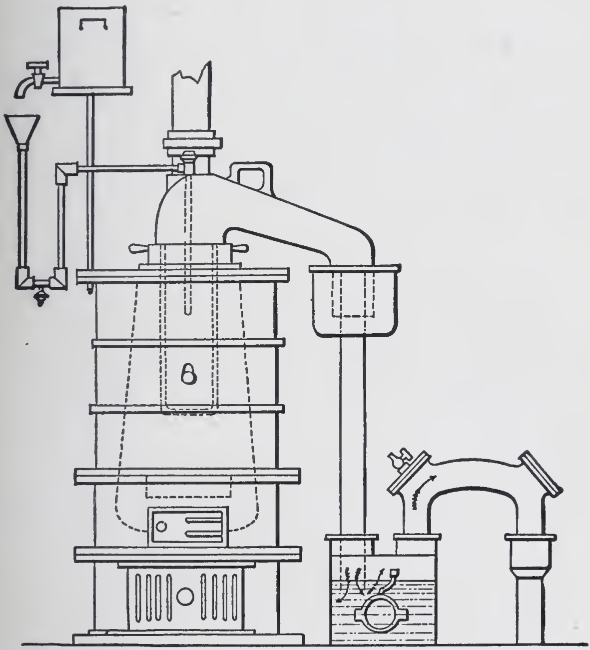

FIG. 34.—"Mansfield" Oil-Gas Plant.

trays contained in a retort resembling that employed for ordinary coal-gas, the vapours and gases are usually passed into a second retort, then "scrubbed" and purified by means of sawdust and ferric oxide, and finally collected. The gas thus obtained is usually compressed by force-pumps into reservoirs and used for lighting railway carriages. It is of high candle-power, often 40 or 50, but when compressed tends to lose some of its illuminating constituents by depositing them as liquids.

"Mansfield oil-gas" is another variety, intended mainly for use in gas engines (Fig. 34).

The following is an analysis of an American sample of oil-gas prepared in a slightly different manner:

	Per cent.
Marsh-gas	44.8
Hydrogen	20.5
Illuminants	28.1
Carbon monoxide	0.6
Carbon dioxide	2.3
Nitrogen	3.5
Oxygen	0.2

Units of heat per cubic foot, 1025.*

WATER-GAS is very largely used as an illuminant in the United States, where anthracite is plentiful and gas coal scarce. It is carburetted by passing it, while hot, over naphtha, then through retorts kept at a white heat by gaseous fuel. The naphtha vapour is thus decomposed and converted into gases of high illuminating power. The mixture as sent to the consumer consists of 70% real water-gas and 30% of gases derived from the naphtha. The gas has a candle-power of 28 to 30 and a strong, penetrating odour. Water-gas is now extensively used as a substitute for coal-gas, and during the last few years a

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* *Jl. Soc. Chem. Indus.*, 1895, p. 136.

number of new plants for its preparation have been erected in various parts of England.

ACETYLENE has been known for many years, but no process by which it could be produced in large quantities was devised until, in 1892, T. L. Willson observed its formation by the action of water upon a substance produced in the electric furnace when lime and carbon were heated together. He saw the importance of such a ready method of obtaining acetylene, and patented the production of calcium carbide by means of the electric furnace.

The reaction by which it is produced is chemically very simple, though it can only be brought about at the enormously high temperature of the electric arc. The equation representing the reaction is as follows:

$$3\,C + CaO = CaC_2 + CO.$$

The process requires the expenditure of a large amount of energy; about 2 or 2½ horse-power working for an hour is consumed in the production of 1 pound of carbide.

Calcium carbide is a crystalline, somewhat metallic-looking, brown or gray solid, which can only be fused in the electric arc. It is permanent in dry air, but is at once attacked by moisture, evolving acetylene. It can be burnt in oxygen or sulphur vapour. In contact with water it evolves torrents of acetylene, leaves a mass of slacked lime, and liberates considerable heat. The amount of gas produced is about 5 cubic feet from each pound of carbide. Thus obtained acetylene invariably contains small quantities of sulphuretted hydrogen, phosphuretted hydrogen, ammonia and free hydrogen, often, also, siliciuretted hydrogen. These substances impart a disagreeable odour to the gas which pure acetylene does not possess and are objectionable, in other respects. Phosphuretted hydrogen and siliciuretted hydrogen are spontaneously inflammable in air, and if they were present in considerable quantities they might insure the ignition of the acetylene on contact with air. Phosphuretted hydrogen by its combustion forms phosphorus pentoxide fumes, and these settle very slowly. To this substance has been attributed the white haze which is sometimes seen in rooms where much acetylene has been burnt.

It is very desirable, therefore, that these impurities should as far as possible be removed. (See page 109.)

Acetylene burns when ignited in air with a brilliantly white flame, giving from 10 to 14 times as much light and about twice as much heat as the same volume of coal-gas, but if burnt from ordinary gas-burners, acetylene gives very smoky flames and not much light. In order to get the best effects it is necessary to use specially constructed burners and generally a slightly higher pressure than that of ordinary coal-gas. Acetylene is a colourless gas with a smell when pure, which is described as pleasant and ethereal. The gas is slightly lighter than air, being 13 times as heavy as hydrogen (the density of air being 14.4).

It is soluble in water, alcohol, benzene, chloroform, acetic acid or acetone.

One vol. of	water	dissolves about	1	vol. of acetylene.
“ “ “	paraffine	“ “	1.5	“ “
“ “ “	benzene	“ “	4	“ “
“ “ “	chloroform	“ “	4	“ “
“ “ “	alcohol	“ “	6	“ “
“ “ “	acetone	“ “	31	“ “
“ “ “	brine	“ “	0.05	“ “

As will be seen from the above table, brine dissolves very little of the gas, and would, therefore, be the most economical liquid to use in a gas-holder. The great solubility of acetylene in acetone is of importance, for, as in all cases of solution of gases in liquids, the amount of acetylene dissolved is proportional to the pressure, and, therefore, by bringing pressure to bear upon the two a quantity of acetylene which would occupy about 300 volumes at the ordinary pressure can be dissolved in 1 volume of acetone. Hence it was proposed to render acetylene conveniently portable by compressing it into acetone. Unfortunately, however, the solution, which easily evolves its acetylene when the pressure is relieved, is not believed to be much safer than liquid acetylene itself. (See below.) The gas can be liquefied by the combined effects of cold and pressure, the actual pressure required varying with the temperature.

Pressure Exerted by Liquid Acetylene.

At	—82° C.	(—115.6° F.)......	1 atmosphere.
"	0° C.	(32° F.)......	22 "
"	15° C.	(59° F.)......	30 "
"	37° C.	(98.6° F.)......	68 "

Liquid acetylene cannot exist at temperatures above 37° C. (98.6° F.), however great the pressure brought to bear upon it. This temperature is called the *critical temperature.*

Berthelot and Vieille* have shown that actylene, existing at any pressure greater than two atmospheres, is wholly decomposed into its constituents if a portion of it be heated by means of a hot platinum wire or by the explosion of a small amount of any detonator. This decomposition is attended with a sudden development of heat and consequent production of high pressure. In the case of liquid acetylene they estimate the pressure exerted by the explosion at 4600 to 6690 atmospheres, which is greater than any envelope could be expected to stand, be-

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* *Jl. Soc. Chem. Ind.*, 1896, p. 793.

ing similar to that exerted by gunpowder when fired in a space which it fills. Thus it is seen that liquefied or even compressed acetylene is a very dangerous substance. Several fatal accidents have occurred on the continent and in the United States, where makers prepared and sold the liquefied gas. Its use or preparation has been prohibited in this country.

In England acetylene is now kept or generated in such a way that its pressure never exceeds that of the atmosphere by more than a few inches of water.

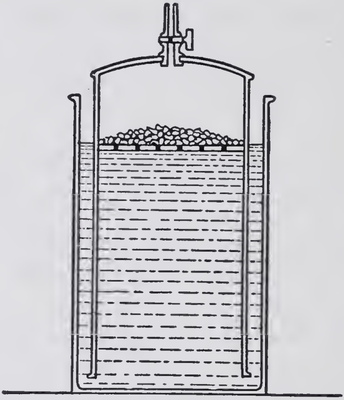

FIG. 35.—Simple Acetylenc Generator.

In small private installations various forms of *automatic* generators are used in which the quantity of acetylene stored is never very large, the gas being produced as required; the gas-holder in such generators has a comparatively small capacity and serves only to regulate the pressure and to compensate for variations of either supply or consumption. For small quantities of gas a simple form of apparatus suffices (Fig. 35). This generally consists of a bell-shaped gas-holder having a perforated cage or upper compartment in which the calcium carbide is placed. This holder fits easily into an open cylinder which is partly filled with water. When the water and carbide are allowed to come in contact acetylene is evolved, collects in the gas-holder and eventually by its buoyancy causes the latter to rise, and thus by lifting the carbide out of the water checks the evolution of gas. When the gas is allowed to issue, the gas-holder gradually sinks until the carbide again comes in contact with the water, and so produces a fresh evolution of acetylene.

Such an apparatus serves excellently when only one or two burners are to be supplied, *e.g.*, for optical lantern purposes, but for house illumination a larger apparatus and one more under control is required. Acetylene generators have of late been favourite subjects for inventors' ingenuity, and numerous patents have been taken out in connection with them. It is quite impossible to describe the various forms, but they usually embody one of three methods of producing the reaction between water and calcium carbide.

(1) Where a limited amount of water is allowed to gradually come in contact with the main mass of carbide.

(2) Where both carbide and water are present in considerable quantity and their contact is brought about by change of level (as in the simple generator just described).

(3) Where the carbide in small fragments is gradually added to a large quantity of water.

Since a considerable evolution of heat is produced when the carbide and water react, it is obvious that the last method is the one which will maintain the most constant temperature, while the first one will be very liable to produce a high temperature. It is on several grounds desirable to keep the temperature low, so that the last method would appear to be the best, but, unfortunately, it is not easy to carry out in practice, and the first method, or a combination of it and the second one, is generally adopted. The gas should be well washed, since this serves to remove some of its objectionable impurities, but intimate contact with large volumes of water is attended with considerable loss of acetylene on account of the solubility of the gas.

Acetylene, like other inflammable gases, will explode when mixed with air and fired. The firing of such a mixture requires that a portion of it should be raised to above a certain temperature. The temperature is, in the case of acetylene and air, about 480° C. (900° F.), being much lower than with any other common inflammable gas.

Temperatures of Ignition of Various Gases in Air.*

Acetylene	480° C.	or	900° F.
Ethylene	580° C.	"	1044° F.
Hydrogen	650° C.	"	1202° F.
Marsh-gas	667° C.	"	1233° F.
Carbon monoxide	700° C.	"	1292° F.
Coal-gas	648° C.	"	1198° F.
Sulphuretted hydrogen	260° C.	"	502° F.

A glowing splint of wood or a brightly glowing cigar or pipe would thus be hot enough to ignite a mixture of acetylene, though unable to set fire to coal-gas and air. Acetylene is consequently more liable to cause explosion than coal-gas.

There is another respect in which acetylene is more dangerous than coal-gas—in the much greater range of

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* These temperatures vary somewhat according to circumstances, *e.g.*, pressure, the nature of the walls of the containing vessel, the state of rest or motion of the gas, etc.

variation in the proportions of gas and air which are capable of exploding.

The following table shows the limits between which explosions may occur:*

All mixtures with air containing from—

Per cent.				
3	to	82	of	acetylene.
5	“	80	“	hydrogen.
13	“	75	“	carbon monoxide.
5	“	17	“	marsh-gas.
4	“	22	“	ethylene.
7	“	29	“	coal-gas.

The violence of an explosion depends partly upon the amount of heat and consequent expansion produced by the chemical union to which the explosion is due and partly upon the rate at which the explosion propagates itself. If the rate of propagation be slow the gas has time to force its way gradually outward, and part of it has cooled down before the other portion becomes hot. On the other hand, when the rate of propagation is high the pressure produced is great, because the gas has not time to get away before the whole mass has exploded. Acetylene with air forms mixtures, in some of which the velocity of propagation is much higher than in the case of other gases.

This is seen clearly in the curves in Fig. 36, which gives the connection between the composition of various mixtures and the velocity of propagation of the inflammation. The maximum velocity (about 6½ yards per second) is possessed by a mixture of 10 volumes of acetylene and 90 volumes of air; the maximum in the case of coal-gas (about 1¼ yards per second) being obtained with about 17 of gas to 83 of air.

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* Clowes, *Jl. Soc. Chem. Ind.*, 1896, p. 793; Bunte, loc. cit.

It should be pointed out in this connection that although a mixture of 10 or 12 volumes of air to 1 volume of acetylene yields, apparently, the most explosive mixture possible, yet, under certain circumstances, a more violent explosion may occur with a gas containing a much larger proportion of acetylene. This has been shown by Gerdes, who gives the following numbers as the results of firing large volumes of air and acetylene in a closed space:

Percentage of acetylene in mixture.	Pressure, in atmospheres.
3.7	3.7
5.5	5.5
10.1	11.1
12.5	10.6
16.6	7.2
33.0	18.4
50.0	20.3
66.0	10.0
80.0	6.3

It will be noticed that there are two maxima, one when the mixture contains 10% of acetylene, where, as has been shown above, is the highest velocity of propagation, and the other at 50%. The latter maximum is explained by assuming that, at the moment of the explosion, the carbon, which subsequently separates as a solid, is in the form of vapour.

Another and more probable explanation is that the ordinary slow explosion, starting from the firing place, travels at first with a velocity of about 8 or 9 inches per second, generating heat and, therefore, producing pressure; that this pressure acts upon the rest of the gaseous mixtures so that the temperature approaches that of ignition (480° C.), or even that of the decomposition of acetylene (780° C.). When either of these points is reached explosion commences at all points of the mixture at once with a consequently sudden expansion. It is known that in certain mixtures the explosion travels for some distance with its usual slow velocity, then increases its speed very rapidly and traverses the rest of the mixture with a velocity equal to that of sound (nearly 400 yards per second). In this case, the first portion of the inflammation of the mixture sets up an area of compression which, travelling with the velocity of sound, determines the inflammation of the gas as it passes, if the heating effect of the compression be sufficiently great.

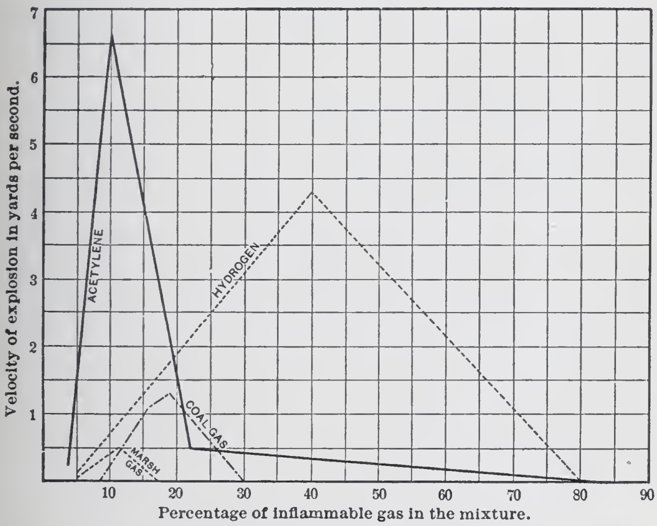

FIG. 36.—Curves showing Velocity of Explosion in Various Mixtures of Inflammable Gases with Air.

The chief dangers attending the use of acetylene are, therefore—

(1) Those incidental to the storing and handling of calcium carbide, arising mainly from the action of water and water vapour upon it.

Calcium carbide ought to be kept in air-tight metal cases and every precaution taken to prevent its contact with water or damp air. If the action of water on the carbide took place under such circumstances that the gas evolved could not escape freely, then pressure (dangerous in itself) would be set up, and if the temperature rose sufficiently, the acetylene might explosively decompose, even in the absence of air. Such an explosion would be a very violent one.

The danger of having any considerable quantity of carbide stored in open casks or otherwise exposed to the air, is sufficiently obvious without detailed mention.

(2) Those connected with acetylene itself.

These include all risks incidental to coal-gas or other inflammable gas and are slightly greater for two reasons: (a) The much lower ignition temperature of acetylene. (b) The unusually wide limits between which acetylene and air form an explosive mixture. Both these have already been fully explained.

Against these disadvantages are several facts which serve to lessen their importance—

(1) The smaller quantity of acetylene which would escape into the air in the event of a burner tap being left open; for the same amount of light as is given by coal-gas about one-tenth or less of acetylene is required.

(2) The smaller mains which serve to carry the gas; the pipe need only be about one-third the diameter of a gas main and, in the event of accidental fracture or melting of the pipe, would deliver about one-tenth the quantity of gas.

(3) The strong odour (due mainly to phosphuretted

hydrogen) enables a very small escape of gas to be detected.

The dangers connected with the use of liquid acetylene have not been discussed at length; indeed, they are so great as to be absolutely prohibitory.

Considerable attention is being paid to the removal of the impurities from acetylene. The most objectionable impurities, it will be remembered, are—

(1) Phosphuretted hydrogen.
(2) Sulphuretted hydrogen.
(3) Ammonia.
(4) Siliciuretted hydrogen.

Nos. 2 and 3 can be almost completely removed by washing the gas with water; No. 4 is not often present in sufficient quantities to be of much importance. No. 1 is the most important impurity. There are several plans in use for its removal—

(1) *Frank's Method.*—In this the absorbent material is cuprous or cupric chloride in the presence of hydrochloric acid; impurities 1, 2 and 3 are all removed, but it is necessary, afterwards, to remove the hydrochloric acid gas from the acetylene by means of lime.

(2) *Ullmann's Method.*—In which chromic acid is used; this destroys impurities 1, 2 and 4 and absorbs the ammonia.

(3) *Lunge's Method.*—Where bleaching powder or chloride of lime is employed. It is desirable in this case to remove the ammonia before the gas reaches the purifier, otherwise a highly explosive substance, chloride of nitrogen, may be formed. Explosions from this cause have occurred.

The following analyses of acetylene from various kinds of carbide may be of interest (quoted by Lewes, Cantor Lectures, Dec., 1898):

	American.	German.	Swiss.	English.	French.
Phosphuretted hydrogen..	0.05	0.03	0.03	0.138	0.045
Sulphuretted hydrogen...	0.08	0.07	0.10	0.064	0.048
Ammonia	0.08	0.07	0.11	....	....
Hydrogen	0.09	0.07	0.16	....	....
Nitrogen	0.42	0.20	0.34	....	....
Oxygen	0.87	0.55	0.63	....	....
Acetylene	98.41	99.01	98.63	....	....

THE ELECTRIC LIGHT.—The reader is referred to one of the numerous text-books on electricity for the fundamental principles of the science. Only a very short account of the subject can be given here.

Electricity is generated either from a battery, in which chemical action is the source of energy, or more generally from a dynamo, in which mechanical energy derived either from steam, gas or oil engines, or from water power, is drawn upon to supply electricity.

Batteries are of two kinds, *primary,* in which the chemical action is not easily reversible and which, therefore, require renewal of the portions which undergo change (in most cases, zinc plates and sulphuric acid are the two principal substances taking part in the chemical action, and when they are converted into zinc sulphate, it is necessary to replace them by fresh quantities of acid and metal), and *secondary,* in which the chemical changes occurring may be reversed by the action of an electric current from external sources. A secondary battery or *accumulator* is often used for electric lighting.

An accumulator generally consists of plates of lead so arranged as to expose a large surface, immersed in dilute sulphuric acid. One of the plates is encrusted with a thick layer of peroxide of lead, the other one being clean. On connecting these two plates by a wire, a current of electricity flows and the previously clean lead becomes corroded, while the peroxide is gradually reduced to the state of monoxide of lead. When this change is complete the accumulator is discharged, but can be recharged by means of an electric current, *e.g.*, from a dynamo, when the plates are restored to their original condition.

Although the number of modifications of the dynamo is very considerable, there are two chief varieties—"continuous current" and "alternating current." These terms are almost self-explanatory.

The current produced in any of the above ways is conveyed to the electric lamps by *"leads,"* generally made of copper, this metal being used on account of its good conductivity. A current of electricity may be roughly compared to a stream of water flowing through a pipe. The quantity which flows through depends upon two values—the diameter of the pipe and the head of water. So in the case of electricity the quantity flowing depends upon the conductivity of the wire and the electromotive force of the current. The conductivity of a wire depends partly upon its diameter and partly upon the material of which it is made.

Whenever a current flows through a conductor a certain amount of resistance is offered by the conductor and the flow of the current is impeded, in a manner analogous to the friction offered by a pipe to the water flowing through it. This action gives rise to the production of heat. If the resistance be small, as in the case of thick wires of pure copper, very little heating is produced; on the other hand, where the resistance is large considerable heating results. In an incandescent lamp, for example, the carbon filament offers considerable resistance, and so is greatly heated by the flow of electricity through it. The leads, therefore, should be as large as possible, consistent with economy.

The current which flows through a circuit is directly proportional to the electromotive force, and inversely proportional to the total resistance, or, in symbols—

$$C = \frac{E}{R} \text{ also heat produced } = CE = RC^2,$$

where C represents the quantity of electricity passing per unit time, E the electromotive force and R the total resistance of the circuit.

C is measured in "Amperes," E in "Volts" and R in "Ohms."

In order to use electricity economically for lighting, it is obviously desirable to make the resistance of the battery and leads as small as possible so as to get little heating effect developed there, and to concentrate all the resistance of the circuit in the lamps. The leads are constructed of such a size as to be quite capable of carrying any current which the battery or dynamo can produce so long as there is in the circuit the high resistance of the lamps; if, however, this high resistance be taken out of the circuit, the amount of current which can flow through the leads is then enormously increased and their temperature is raised, it may be to an extent which will destroy or even ignite their insulation.

This occurs when the wires are "short circuited," *i.e.*, when they are electrically connected by any substance not offering much resistance, and such an accident represents almost the whole risk of fire connected with electric lighting. In order to obviate this risk and to save the lamps from destruction in the event of any sudden increase in the amount of current sent through any particular circuit, the leads are provided with "cut-outs" consisting of short pieces of lead or tin wire of such size as to carry the usual current, but still of much greater resistance than the rest of the leads, so that when the amount of electricity passing in the circuit rises to a dangerous point they fuse and break, thus stopping all current.

In "arc" lighting an obvious source of danger is the dropping of fragments of carbon from the terminals. This is guarded against by the use of globes, which are further protected by wire netting.

Some other sources of danger may be mentioned: the crossing of the leads should be avoided as much as possible, and, if really necessary, additional insulation should be used, *e.g.*, by placing mica between them.

Switches, which are used for making or breaking the circuit, should be so arranged that they will only rest when either fully on or off.; if they could be left in an intermediate position there is danger of the current "arcing" across.

It would be beyond the scope of the present work to give details of electric light installations; the reader is referred to the "Phœnix" Fire Office Rules, papers in the reports of the Yorkshire Insurance Institute, 1889-90, 1891-92, and to Sir David Salomon's book on Electric Light Installations (Whittaker & Co.) for practical information.

In conclusion we may quote some extracts from the rules and regulations drawn up by the society of Telegraphic Engineers and Electricians, with especial reference to the reduction of fire risks to a minimum.

Conductors.—All leads must have a sectional area sufficent to allow of their carrying at least twice the current that it is proposed to send through without their temperature rising to 150° F. (65.5° C.). The insulating material should be damp-proof and should not soften below 170° F. (76.5° C.).

The leads should be kept as far apart as circumstances will allow, in order to lessen the risk of short-circuiting.

All joints must be carefully made to prevent heat being generated at them as the current passes. Under all circumstances complete metallic circuits should be employed. Gas fittings and water pipes should never be employed as leads, and particular care should be taken to prevent any part of the circuit being "earthed."

Switches must fulfil the conditions already alluded to and must be provided with insulated handles. They should be mounted on incombustible bases, *e.g.*, slate, earthenware or porcelain.

Cut-outs must be provided, both on the main circuit and at every branch of a smaller lead from the main. They must be so arranged that molten metal cannot drop upon any wire or combustible material, so as to produce either a short-circuit or ignition.

CHAPTER VII.

SOME INORGANIC INDUSTRIES.

Sulphur and Sulphuric Acid—Nitric Acid and Nitrates—Chlorates—Phosphorus and Matches.

SULPHUR or *brimstone* is obtained from various sources, the principal being—

(1) Native sulphur. This occurs largely in Sicily; near Vesuvius; in Mexico, in Iceland and in many other volcanic regions.

(2) Iron pyrites, FeS_2.

(3) Alkali waste and the spent oxide of gas works.

Native sulphur occurs mixed with gypsum and other mineral substances and is purified by liquation, *i.e.*, by heating the crude material, when the sulphur melts and runs away from the earthy, infusible "gangue." The product is often refined by distillation, when "flowers of sulphur" are obtained if the cooling be rapid, or "roll sulphur," if the cooling be more gradual. Occasionally it is extracted from its ores by means of carbon disulphide, in which it is very soluble; an operation necessarily attended with considerable risks.

From *iron pyrites*, sulphur is obtained by distillation, usually in fire-clay retorts, not heated too highly, otherwise the iron sulphide left fuses and sinks into the retorts and destroys them. Theoretically 26% of sulphur may be obtained by distillation from pyrites, leaving a residue of iron sulphide, FeS. In practice, owing to the low temperature employed, only 13% or 14% is obtained. Sulphur from this source is often contaminated with arsenic.

From *vat* or *alkali waste,* which consists mainly of calcium sulphide, the sulphur is recovered by means of the "Chance" process, which consists in treatment of the waste, ground to a cream in water, with carbon dioxide, obtained from limestone. Sulphuretted hydrogen gas is evolved and by an ingenious method of working can be obtained in a fairly concentrated state. From the sulphuretted hydrogen, sulphur can be obtained by burning it in a limited supply of air, in the "Claus" kiln—

$$H_2S + O = H_2O + S.$$

The sulphur vapour, with the steam formed by the combustion of the hydrogen, passes into chambers, where it condenses and is thus obtained in the solid state.

The *spent oxide* from gas purification can be made to yield its sulphur by distillation, but more generally it is heated in air so as to form sulphur dioxide for use in sulphuric acid manufacture. Spent oxide contains a variable amount of sulphur, sometimes as high as 55%, but more generally 30-40%.

Sulphur is a brittle, light yellow solid, which melts at 113° C. (235.4° F.), forming a thin, yellow liquid; on heating, this liquid darkens and becomes more and more viscid; as the temperature rises it again becomes more fluid, though remaining dark in colour; finally, at about 440° C. (824° F.), it boils, giving a reddish vapour, which, if quickly cooled, yields "flowers of sulphur."

Sulphur ignites readily, its ignition temperature being about 250° C. (482° F.). Its flame is comparatively cool, the theoretical temperature being about 1900° C., but as actually measured, much lower.

Sulphur is capable of existence in three or more modifications which differ considerably in physical properties. (See any text-book of chemistry.)

It is largely used in the manufacture of gunpowder and matches, for "sulphuring" wines and hops, for disinfecting and bleaching (in these cases the active substance is really sulphur dioxide, formed by burning sulphur in air), in the preparations of many sulphur compounds, *e.g.,* carbon disulphide, sulphur chloride, vermilion (sulphide of mercury), mosaic gold (sulphide of tin) and in vulcanising caoutchouc and gutta percha.

SULPHUROUS ACID, or, more correctly, *sulphur dioxide,* SO_2, is made by burning sulphur, iron pyrites or other metallic sulphide in air.

It is a colourless gas, possessing a most suffocating smell and acting as a violent poison. It is not combustible, nor will it support the combustion of ordinary inflammable substances.

Sulphur dioxide is sometimes made as required by burning sulphur in air, but is now largely supplied in the liquid state, for it is readily liquefied by pressure or cold. At the ordinary temperature a pressure of 2½ atmospheres is required, and the colourless liquid (of sp. gr. 1.4) obtained, boils at —10° C. (14° F.). The gas is soluble in water, 40 or 50 volumes dissolving in 1 volume of water.

Sulphur dioxide is chiefly used because of its disinfecting, antiseptic and bleaching powers. It has been employed for extinguishing fires, especially in chimneys. (See Chap. XV.) It is used for bleaching such substances as cannot be bleached by chlorine, *e.g.,* silk, wool, feathers, sponges, glue, straw, etc. It is largely used as a disinfectant and as an antiseptic, also for preserving fruit, wines, meat, syrups, etc.

The *sulphites,* as the salts derived from it are called, are possessed of similar antiseptic properties, and are often employed for like purposes. The more common sulphites are sodium sulphite, $Na_2\ SO_3\ 7\ H_2O$, sodium bisulphite, $NaHSO_3$, and calcium bisulphite, $Ca\ (HSO_3)_2$.

SULPHURIC ACID.—The manufacture of sulphuric acid is one of the most important processes in industrial chemistry, but is not attended with any particular fire risks. The method almost always adopted in England, known as the "leaden chamber" or English process, consists essentially in the production of sulphur dioxide by the burning of pyrites or sulphur, and the oxidation of this to sulphur trioxide. This oxidation is effected by the oxygen of the air through the intervention of oxides of nitrogen, and in the presence of water. Nitrogen peroxide is the main agent in bringing about the conversion—

$$\underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{SO_2} + \underset{\substack{\text{Nitrogen}\\\text{peroxide.}}}{NO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} + \underset{\substack{\text{Nitric}\\\text{oxide.}}}{NO.}$$

The nitrogen peroxide is thereby reduced to nitric oxide.

This latter body, by contact with air, is reconverted into the peroxide, which can again oxidise an additional quantity of sulphur dioxide. Thus the process goes on, the oxides of nitrogen acting as carriers of oxygen from the air. Theoretically, therefore, a small quantity of nitrogen peroxide is able to convert any amount of sulphur dioxide into sulphuric acid. In practice it is found that there is a consumption of oxides of nitrogen; the loss is due partly to the fact that some are mechanically swept out of the sphere of action by the current of gases and partly to the reduction of some of the nitrogen peroxide to nitrous oxide, N_2O, or even to nitrogen, neither of which can take up oxygen from the air.

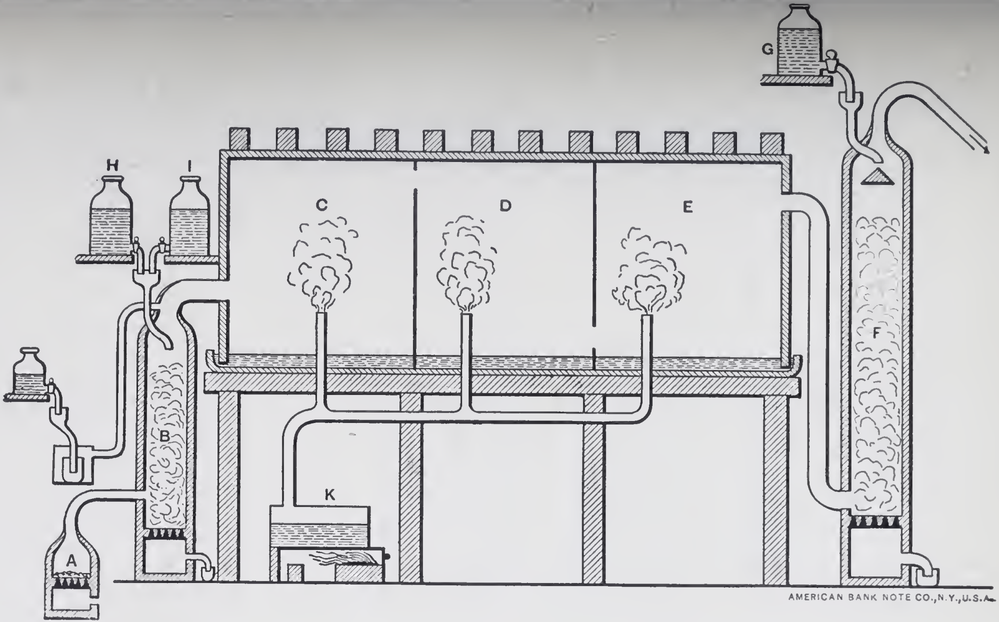

FIG. 37.—Sulphuric Acid Plant. A, Pyrites Burner, the waste heat of which heats the Nitre Pot; B, the Glover Tower, where the Nitrated Acid H from F is mixed with Dilute Chamber Acid I, and so gives off its Oxides of Nitrogen to the Sulphur Dioxide; C, D, and E, the Leader Chambers; F, the Gay Lussac Tower, where the Oxides of Nitrogen are absorbed in strong Sulphuric Acid stored in G.

The operations are carried out in large chambers made by "burning" sheets of lead together. This burning consists in fusing the edges together by means of a blowpipe and thus avoiding the use of solder of any kind, which would cause corrosion. The top, sides and ends of the chamber are thus "autogenously" soldered together and the whole structure is supported on an external frame of timber, to which it is fastened by leaden straps also "burnt" on. The bottom of the chamber is formed of a large tray or saucer of lead, the edges, turned up 12 or 15 inches, being outside the rest of the chamber. The tray is kept partially full of acid, and so seals the chamber from the air. These chambers are often about 100 by 30 feet and 16 to 20 feet high; two, three or four of them are used (Fig. 37).

The sulphur or pyrites is burnt in specially constructed kilns, and an excess of air is drawn in through the kilns. The reactions are—

$$\underset{\text{Sulphur.}}{S} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Sulphur}\\\text{dioxide}}}{SO_2},$$

$$\text{or } \underset{\text{Pyrites.}}{4\,FeS_2} + \underset{\text{Oxygen.}}{11\,O_2} = \underset{\text{Iron oxide.}}{2\,Fe_2O_3} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{8\,SO_2}.$$

The sulphur dioxide, thus formed, diluted with a large amount of nitrogen and an excess of air, is conveyed to the chambers, and on its way passes the "nitre pots." These consist of cast-iron, cylindrical vessels in which nitrate of soda, $NaNO_3$, is decomposed by sulphuric acid, thus giving rise to nitric acid, which reacts with the sulphur dioxide, thus—

$$\underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{3\,SO_2} + \underset{\substack{\text{Nitric}\\\text{acid}}}{2\,HNO_3} + \underset{\text{Water.}}{2\,H_2O} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3\,H_2SO_4} + \underset{\substack{\text{Nitric}\\\text{oxide.}}}{2\,NO}.$$

The nitric oxide so formed combines with the oxygen of the air to form nitrogen peroxide, NO_2—

$$\underset{\text{Nitric oxide.}}{2\ NO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Nitrogen peroxide.}}{2\ NO_2.}$$

The peroxide is then reduced again by the sulphur dioxide—

$$\underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{SO_2} + \underset{\substack{\text{Nitrogen}\\\text{peroxide.}}}{NO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} + \underset{\substack{\text{Nitric}\\\text{oxide.}}}{NO.}$$

The sulphuric acid exists in the chambers at first as a mist, which gradually settles to the bottom and becomes a liquid. It must not be allowed to become stronger than of sp. gr. 1.6, otherwise it attacks the lead and absorbs oxides of nitrogen. The acid is therefore run off from the chamber when it reaches this strength and is concentrated in leaden vessels until it attains a sp. gr. of 1.72, beyond which it cannot be taken without acting considerably upon the lead. Acid of this strength suffices for many purposes and is often called B. O. V. (brown oil of vitriol).

If required stronger than this, it is boiled down in glass or platinum retorts. The glass retorts are large, about 3 feet deep and 2 feet in diameter, holding some 20 gallons; they are heated in sand trays and often crack.

The breakage of a retort leads not only to the loss of the contents, but very often to the destruction of the neighbouring retorts, if several are placed in the same shed, as is usually the case. The air is filled with the irritating vapours of sulphuric acid and the workmen are unable to enter the shed until the fumes have dispersed. In order to avoid the annoyance and loss occasioned by the fracture to which glass is liable, retorts made of platinum are sometimes employed; these are exceedingly costly (platinum costing from 50s.-80s. per ounce) and consequently are kept going continuously. The platinum is slightly attacked by the acid, especially if the latter contains nitrous fumes. Loss of platinum is sometimes prevented by lining the retorts with gold. The strong acid obtained by concentration in this way is known as D. O. V. (double oil of vitriol) and has a specific gravity of 1.84.

Sulphuric acid is a heavy, oily, odourless liquid, having a strong affinity for water, and producing a considerable rise of temperature when diluted; 1 pound of acid mixed with about one-fifth of its weight of water evolves 70 thermal units, *i.e.*, enough heat to raise the temperature of 1 pound of water through 70° C. Since sulphuric acid has a much lower specific heat than water, its temperature will thereby be raised by more than 70° C., often, indeed, to above the boiling point of water. The dilution of sulphuric acid therefore requires care. The acid should always be poured into the water, with constant stirring, and never the reverse.

In consequence of its strong affinity for water, sulphuric acid will often remove the hydrogen and oxygen from organic substances, leaving a residue consisting mainly of carbon. It therefore chars many organic bodies, *e.g.*, cellulose, of which vegetable fibre is largely composed, sugar, starch, etc. If the organic substance be previously mixed with a powerful oxidising agent, *e.g.*, chlorate of potash or nitrate of soda, the contact with sulphuric acid is often accompanied by rapid combustion, so as to practically constitute an explosion.

Another property of the acid which leads to danger of fire is its action upon metals like zinc or iron. In the presence of water these metals liberate hydrogen from sulphuric acid, and hydrogen, as already stated (Chap. IV.), forms a very explosive mixture with air.

Nitric acid is obtained by the action of strong sulphuric acid upon nitrate of soda, a salt found in large quantities in Peru, Chili and Bolivia as an efflorescence on the soil.

The preparation is usually carried out in cylindrical retorts of cast-iron, for though both sulphuric acid and nitric acid, when diluted, attack iron fiercely, they are practically without action upon it when concentrated. The reactions are—

$$(1)\ \underset{\text{Sodium nitrate.}}{NaNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\substack{\text{Acid}\\ \text{sodium sulphate.}}}{NaHSO_4} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{HNO_3}.$$

$$(2)\ \underset{\text{Sodium nitrate.}}{NaNO_3} + \underset{\substack{\text{Acid}\\ \text{sodium sulphate.}}}{NaHSO_4} = \underset{\substack{\text{Sodium}\\ \text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{HNO_3}.$$

The vapours of nitric acid are condensed, generally in earthenware vessels, and constitute the "aqua fortis" of commerce. This contains 60-67% of HNO_3 and has a sp. gr. of about 1.4; it is often coloured yellow or red from the presence of lower oxides of nitrogen. A stronger acid, almost pure, is obtained by distilling ordinary aqua fortis with strong sulphuric acid, and has a sp. gr. which may be as high as 1.55 (97% HNO_3).

Nitric acid is a corrosive liquid attacking organic matter, oxidising it, and in the case of many nitrogenous bodies, giving rise to an intensely yellow colouration. Thus the skin, wool, horn, feathers, etc., are stained yellow, and if contact with the acid be prolonged, are destroyed.

Strong nitric acid, if brought into contact with dry organic matter, oxidises it rapidly and evolves heat. In many cases, fire results from such contact. This is particularly liable to occur with dry straw, sawdust, etc., so that great precautions should be taken to prevent the acid being spilled upon packing materials, like those mentioned.

Nitric acid is used in a very large number of industrial operations, *e.g.*, in dyeing, in the preparations of lacquers, in the manufacture of picric acid, nitrobenzol, etc., in the manufacture of many coal-tar colours, of many explosives, as gun-cotton, fulminate of mercury, nitroglycerine, etc., etc.

The nitrates, as the compounds derived from nitric acid by the replacement of its hydrogen by a metal are called, are, like the acid itself, powerful oxidising agents. They therefore require considerable care in handling, not because they have any tendency to burn in air, but because of their liability, when mixed with oxidisable matter, to produce its oxidation and consequent ignition and inflammation. Slight friction of a nitrate against any dry inflammable matter, *e.g.*, wood, may be sufficient to start a fire. If the nitrate and inflammable substance be intimately mixed there results a violently explosive combination. Gunpowder is such a mixture.

Nitrates which are specially important on account of their common occurrence are—

Sodium nitrate, $NaNO_3$, largely used as a manure and in the preparation of nitric acid, sometimes in the manufacture of mining powder.

Potassium nitrate, KNO_3, "saltpetre" or "nitre," used for preserving certain articles of food, in the manufacture of matches and of gunpowder.

Lead nitrate, $Pb(NO_3)_2$, used in the preparation of pigments.

Ammonium nitrate, NH_4NO_3, used in the preparation of nitrous oxide, the "gas" of the dentists, and in certain explosives.

The so-called "nitrate of iron" of the dyer, prepared by oxidising "copperas" (ferrous sulphate) with nitric acid, consists mainly of ferric sulphate.

CHLORATES are compounds resembling, in many of their properties, the nitrates. Potassium chlorate is the only one commonly met with, though recently sodium chlorate is being made on the large scale.

Potassium chlorate is largely used in the manufacture of fireworks, matches and percussion caps, in the production of aniline black and in the preparation of other coal-tar colours. It is also used in chemical laboratories and often for the preparation of oxygen. It is an extremely powerful oxidising agent, and if subjected to pressure in contact with combustible substances often gives rise to explosive ignition. Mixtures of organic matter and chlorates are extremely dangerous, as they are easily ignited by slight pressure or friction and instantly inflamed by contact with strong sulphuric acid.

Chlorates, like nitrates, must therefore be treated with care, for if they be scattered about a wooden floor or mixed with sawdust, bran, straw, etc., they may readily produce inflammation by slight friction or pressure.*

A chlorate is decomposed by strong sulphuric acid with the evolution of an explosive gas, chlorine peroxide, a substance possessing a characteristic odour.

PHOSPHORUS was discovered by Brand, of Hamburg, in 1674, and attracted great attention from the early chemists on account of its remarkable properties. It was originally obtained from urine, in which it is present to the extent of about 1%. Scheele, in 1771, discovered a method by which it could be obtained from bones, which contain a much larger quantity; about 15% of phosphorus

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* The violent explosion at St. Helen's in May, 1899, does not appear to have been caused in this way, as the 150 tons of chlorate were quite free from contamination with organic matter. (See p. 257.)

is found in bone-ash. Of late, mineral phosphates, chiefly phosphates of lime and alumina, have been used as raw materials. The phosphate is first treated with sulphuric acid, which converts the lime into sulphate and sets free the phosphoric acid—

$$\underset{\text{Calcium phosphate.}}{Ca_3P_2O_8} + \underset{\text{Sulphuric acid.}}{3\,H_2SO_4} = \underset{\text{Calcium sulphate.}}{3\,CaSO_4} + \underset{\text{Phosphoric acid.}}{2\,H_3PO_4}.$$

The sulphate of lime is insoluble, the phosphoric acid soluble, in water; they can therefore easily be separated. The solution of phosphoric acid is evaporated to small bulk and mixed with some carbonaceous matter, either sawdust or charcoal powder, then dried and very strongly heated in fire-clay retorts connected by iron or copper pipes to a trough of water.

Phosphorus vapour is expelled and is condensed in the water. The reactions are—

$$(1)\quad \underset{\text{Ortho-phosphoric acid.}}{2\,H_3PO_4} = \underset{\text{Water.}}{2\,H_2O} + \underset{\text{Meta-phosphoric acid.}}{2\,HPO_3}.$$

$$(2)\quad \underset{\text{Meta-phosphoric acid.}}{4\,HPO_3} + \underset{\text{Carbon.}}{12\,C} = \underset{\text{Carbon monoxide.}}{12\,CO} + \underset{\text{Phosphorus.}}{P_4} + \underset{\text{Hydrogen.}}{2\,H_2}.$$

The yield is only about 70% of the theoretical amount. The crude phosphorus obtained is purified, either by melting under water and squeezing through chamois leather or by treating with an acid solution of potassium dichromate. The refined product is then melted and cast into sticks or cheese-shaped masses and packed with water in sealed tins. Formerly the sticks were made by the dangerous and unhealthy plan of sucking the molten phosphorus under hot water into glass tubes by means of the mouth. Sometimes the phosphorus is granulated by allowing it to fall in drops into cold water. Large quantities of phosphorus are often packed in wooden kegs filled with water; these are coated outside with pitch and covered with stout canvas.

Other methods of preparing this substance have been employed.*

Nearly all the phosphorus of the world is made at two or three works, the largest being those of Messrs. Albright & Wilson, Oldbury; and Messrs. Coignet et Fils, Lyons.

Phosphorus is a transparent, colourless or slightly yellow, waxy substance of sp. gr. 1.83. Its most characteristic properties are its extremely ready oxidisability and its power of shining in the dark, when exposed to air.

It has a peculiar odour and its vapour is very poisonous, producing a painful disease of the bones of the face and jaw. By contact with air it produces white fumes of oxide of phosphorus, and a portion of the oxygen of the air is converted into ozone (an active, allotropic form of oxygen, consisting of molecules, each containing three atoms), the phosphorus becoming warm and generally melting and inflaming. It has, therefore, to be preserved under water.

It melts at 44° C. (112° F.) and boils at 290° C. (554° F.). It is almost insoluble in water, slightly soluble in turpentine, many oils and ether, and readily so in sulphur chloride, phosphorus trichloride and carbon disulphide.

Although it shines in the dark in air, it is not luminous in pure oxygen at ordinary pressures, but becomes so at a pressure of about 1-5 of an atmosphere. Its luminosity in air is quenched at once by small quantities of sul-

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* See papers by Readman, *Jl. Soc. Chem. Indus.*, 1890 and 1891.

phuretted hydrogen, turpentine and many other substances.

Phosphorus is extremely poisonous, doses of 1.5 grains being sufficient to cause death.

Its chief uses are in chemical laboratories, in a few metallurgical processes, *e.g.*, the manufacture of phosphor-bronze, in the manufacture of matches and as a rat poison.

Red Phosphorus.—Schrotter, in 1845, found that the ordinary yellow phosphorus could be changed into a very dissimilar substance by the action of heat, without undergoing any change in chemical composition. The change is produced by heating the phosphorus in an atmosphere of nitrogen or carbon dioxide to a temperature of about 250° C. (482° F.) for a long time. The phosphorus becomes converted into a dark red powder of sp. gr. 2.1.

This is totally unlike ordinary phosphorus in nearly all its properties; it is non-inflammable unless it be heated to nearly 300° C. (572° F.), when it changes again into ordinary phosphorus; it is insoluble in carbon disulphide and other solvents, and it is non-poisonous. It may be mixed safely with many oxidising agents, like saltpetre or even potassium dichromate, but explodes violently when rubbed with lead peroxide or potassium chlorate.

Red phosphorus is used in the preparation of certain organic colouring substances, fine chemicals, and in the manufacture of safety matches.

LUCIFER MATCHES are of two kinds, "ordinary," which can be ignited anywhere by friction, and "safety," which ignite only on the prepared surface attached to the boxes containing them. The ordinary matches, far more commonly used than the safety, are made by first preparing the splints, which are cut from straight-grained timber, often Canadian pine, and are made of twice the length of the finished match. The splints are dried, placed in dipping frames, each in a separate groove, and are then submitted to the following processes:

(1) Sulphuring or paraffining.
(2) Dipping.
(3) Drying.
(4) Halving.
(5) Boxing.

The first operation is intended to render the wood more easy to ignite by the flame of the phosphorus mixture. Sulphur was formerly in general use, but latterly it has been almost entirely replaced by paraffine wax, except for matches intended for the use of sailors, who prefer the sulphur matches, as they are not so readily blown out by a wind; the smell of the burning sulphur is, of course, not so objectionable in the open air as it is indoors.

The dipping composition varies considerably, but nearly always contains—

(1) Phosphorus, finely divided or, better, dissolved in carbon disulphide.

(2) An oxidising agent, potassium chlorate or nitrate, red lead, lead nitrate or dioxide, or potassium dichromate.

(3) Cementing or binding materials, gum or glue.

(4) Friction increasers, glass or sand.

(5) Colouring matter; any cheap colour is used.

The mixture of the above with a little water is kept in a semi-fluid state on slabs heated by steam; both ends of the splints are dipped into this paste, the portion which adheres to one end being allowed to set before the frame is turned over to dip the other. The frames are then set aside to dry in a warm, well-ventilated room. The splints are next taken out of the frame and cut in half by means of a knife pivoted at one end, and the matches are put into boxes ready for sale. A similar method is used in the manufacture of wax vestas, where 4 or 6 cotton threads are coated with a mixture of 2 parts stearine and 1 part paraffine wax.

Fires, owing to accidental friction of the matches, are of constant occurrence at a match factory; they are usually of small consequence and are easily quenched by means of sand, which is kept in readiness.

Safety matches, introduced in 1855 by Lundström, are usually made with the oxidising material, potassium nitrate or chlorate, together with some oxidisable substance, often antimony sulphide, and powdered glass in the head of the match while the phosphorus (red) is on the rubber of the box.

The compositions employed vary much, but the following may be taken as typical—

Head composition.	Pts.	Rubber composition.	Pts
Antimony sulphide...	2	Red phosphorus......	2
Potassium chlorate...	2½	Gum arabic	1
Red lead............	3	Powdered glass......	1
Gum arabic..........	4		
Powdered glass, up to	20		

The use of safety matches is to be recommended not only on account of their greater freedom from risk of accidental ignition, but also on account of their non-poisonous character; non-poisonous they are, both in preparation and in use. Denmark and Switzerland have officially recognised the superiority of the safety match by passing acts forbidding the use or manufacture of matches containing ordinary phosphorus.

In order to lessen the risk of the heads of matches falling off while burning, the stems are sometimes treated with solutions of salts like sodium phosphate or tungstate, zinc sulphate, alum, magnesium sulphate, etc., intended to render the wood less inflammable, and thus prevent its burning too rapidly. This plan is often adopted by Swedish and Belgian manufacturers, who export large quantities of safety matches, especially to England.

The match-making industry is an important one in England; it was estimated some years ago that the annual value of the English match manufactures was from £1,500,000 to £2,000,000.*

* *Jl. Soc. Chem. Indus.*, 1887, p. 772.

CHAPTER VIII.

EXPLOSIVES.

Gunpowder — Guncotton — Nitroglycerine — Various Explosives Containing the Two Latter—Other Explosives—Detonators.

An explosive is a substance, solid, liquid or gaseous, a mixture or a compound which can, by chemical action, produce a rapid and considerable expansion, generally by the production of gas or vapour, but, usually, the term "explosive" is applied to a solid or liquid body.

Explosives may be divided into two classes—

(1) Those in which two or more constituents by their interaction evolve heat and gases. Such explosives generally consist of a powerful oxidising agent and one or more oxidisable substances yielding gaseous products when oxidised, *i.e.,* they are mixtures.

(2) Those in which only one chemical compound is present or takes part in the explosion. In this case the substance is *endothermic, i.e.,* one which has absorbed energy in its formation; this energy is evolved in the form of heat in its explosion or decomposition into two or more simpler substances, one or more of which is gaseous.

Gunpowder may be cited as an example of the first class. This substance, formerly the only important explosive and still largely used, consists of an intimate mixture of saltpetre,—the oxidising ingredient, with sulphur and charcoal,—the oxidisable ingredients.

The proportions of the constituents vary—

	Saltpetre.	Sulphur.	Charcoal.
Black gunpowder	75	10	15
Mining powder	65	20	15
Cocoa powder	79	2	19

The saltpetre used is refined by dissolving the ordinary saltpetre in hot water, filtering off any undissolved matter and allowing the solution to cool with constant stirring. Fine crystals, known as "saltpetre flour," are thus obtained, the liquid retaining in solution almost all the impurities originally present in the salt.

The sulphur is generally the Sicilian native roll sulphur; "flowers of sulphur" are never used because of their contamination with traces of sulphuric acid, which would cause the gunpowder to absorb moisture from the air.

The charcoal is prepared with great care, as the properties and qualities of the gunpowder depend very much upon the character of the charcoal used in its preparation. The main point is the temperature at which the wood has been carbonised, for, as shown in the table on page 67, the temperature of ignition of the charcoal is greatly dependent upon this.

The materials are reduced to coarse powder,* weighed out and roughly mixed by means of wooden shovels. They are then taken to incorporating mills, which resemble ordinary mortar mills. Comparatively small quantities (50 or 60 pounds) of the mixture are operated upon, considering the large size of the apparatus (each of the two rollers weighs about 4 tons). The powder is submitted to the action of the mill for from 3 to 8 hours. During the incorporation, ignition of the powder is liable to occur and so each of the mills is provided with a drenching tank placed just above it, often so arranged

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* The grinding of sulphur is attended with some risk, as the friction generates electricity, and sparks sufficiently large to cause ignition may easily be produced.

that an explosion in one mill will automatically overturn not only its own drenching tank, but also those belonging to all the neighbouring mills. The "mill cake" is then "broken down" by passing it through gun-metal rollers, one of which is grooved and the other smooth. The "meal" is then submitted to hydraulic pressure so as to consolidate it into cakes of thickness varying according to the kind of powder desired.

The "press cake," a hard, compact substance, is next granulated by a special mill in which the cake passes through several pairs of toothed gun-metal rollers; the fragments pass down an inclined revolving cylinder provided with a graduated series of apertures through which the powder falls, and are thus sorted into grains of different sizes.

The grains are then polished by rotating them in barrels for some hours, when they glaze each other, or, in the case of the larger grained powders, a small quantity of graphite is added; this gives a high lustre to the powder, and is said to render it less susceptible to the influence of moist air. Finally it is dried by heating in trays in well-ventilated rooms to a temperature varying from 38° C. (100° F.) to 54° C. (129° F.).

It will be seen that the process of manufacturing gunpowder is almost entirely a mechanical one and the risks attending it are only such as proceed from dealing with such an inflammable substance. The greatest care has to be taken to avoid all flame or heat of any kind, and also to ensure the absence from the powder and the machinery of all fragments of hard materials, *e.g.*, iron, grit, etc., which by friction or pressure could give rise to the production of a spark.

For large ordnance, "pebble powder," consisting of irregular cubes, either $\frac{3}{8}$-inch or $1\frac{1}{2}$-inch in size is manufactured. These are cut from the press cake by means of phosphor-bronze knives. Recently pebble powder has been largely replaced by "prismatic powder," which is made by pressing, by hydraulic machinery, coarse-grained powder into hexagonal prisms, about 1 inch high and 1.37 inches in diameter, each prism being perforated by a central hole.

Gunpowder contains everything necessary for its own combustion, and if it be heated to a sufficiently high temperature, decomposition begins and spreads rapidly throughout the mass. The temperature at which explosion commences varies, but is usually about 290° C. (554° F.) for black and 304° C. (579.2° F.) for brown prismatic powder.

The products formed by its explosion are somewhat complex and cannot be satisfactorily represented in a chemical equation. A portion is solid, part of which remains fouling the gun while the greater part is blown into the air in fine particles, giving rise to the smoke, and a portion is gaseous. The usual composition of the solid residue is shown below—

	Pebble.	Sporting.	Mining.	Cocoa.
Potassium carbonate..	59	59	42	78
" sulphate...	13	22	1	22
" sulphide...	19	12	37	none
Sulphur	8	6	14	..
Charcoal	trace	..	3	..
Other substances.....	1	1	3	..

The gases have the following composition—

	Pebble.	Sporting.	Mining.	Cocoa.
Carbon dioxide........	49	50	32	51
Carbon monoxide.....	14	8	34	3
Nitrogen	32	34	19	42
Sulphuretted hydrogen	3	2	7	none
Hydrogen	2	5	7	3
Oxygen and marsh-gas	traces	traces	traces	traces

The pressure produced by gunpowder exploded in a space which it just fills is estimated at 42 tons per square inch. Cocoa powder differs from the other kinds, as will be seen from the above analysis, not only in the products which it yields, but also in that it evolves more heat and less permanent gas than the other varieties—

One gramme yields	Units of heat.	Cubic centimetres of gas.
Cocoa powder	837	198
Sporting	764	241
Pebble	721	278
Mining	517	360

The unit of heat taken in the above table is the amount necessary to raise one gramme of water through 1° C. The temperature at the moment of explosion is calculated as 2200° C. The total energy set free by the explosion of 1 pound of gunpowder is estimated at 500 foot-tons, of which, in modern guns, one-tenth to one-fifth is actually utilised. The explosion of gunpowder is a process of rapid combustion, beginning at a certain point and spreading from thence gradually, though rapidly, throughout the whole quantity. The rapidity with which the inflammation spreads in a mass or charge of gunpowder is the main factor which determines the suddenness and violence of the explosion. It spreads most rapidly in small-grained powder and only very slowly if the grains be large, *e.g.*, in prism powder. The rapidity, too, is greatly affected by the pressure, being greater the greater the pressure, thus in a partial vacuum, inflammation started at the top of a heap is often confined to a few grains and is not communicated to the rest. If a quantity of powder be very gradually heated so that the whole of it approaches the temperature of ignition before inflammation starts, then the explosion which results when ignition occurs, is incomparably more violent than usual, resembling, rather, a detonation, such as happens under certain conditions with guncotton or nitroglycerine.

Gunpowder has lately, to a great extent, been replaced by other more powerful explosives. Many of these are made up of mixtures whose principal ingredients are guncotton and nitroglycerine. It is advisable, therefore, to describe the preparation and properties of these two substances before mentioning the commercial products containing them.

GUNCOTTON.

Guncotton was discovered in 1845 by Schonbein. It is made by acting upon purified cotton waste with a mixture of 1 part of strong nitric acid (sp. gr. 1.5) and 3 parts sulphuric acid (sp. gr. 1.85). The operation is conducted in cast-iron pots, each holding about 2 cwts. of mixed acid. The cotton, after about 5 minutes' immersion, is removed and allowed to remain with the adhering acid for 24 hours in earthen jars surrounded by cold water. The excess of acid is removed by means of a centrifugal machine or hydro-extractor and thorough washing in a large quantity of water. The cotton is then pulped by a machine similar to those used in converting rags into paper. After being again thoroughly washed, the pulp is made into slabs or cylinders, by means of hydraulic pressure, in moulds provided with bottoms of fine gauze.

The main quantity of guncotton is kept in a moist state, but those portions which are intended as "primers," *i.e.,* those portions of a charge which by their detonation cause explosion in the remainder, are dried carefully at a low temperature.

Cotton consists essentially of cellulose, $C_6H_{10}O_5$. This by the action of strong nitric acid is converted into cellulose tri-nitrate—

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{3\,HNO_3} = \underset{\text{Guncotton.}}{C_6H_7O_2(NO_3)_3} + \underset{\text{Water.}}{3\,H_2O}.$$

The sulphuric acid absorbs the water as fast as it is formed, and so serves to prevent the formation of other nitro-celluloses, like $C_6H_8(NO_2)_2O_5$. In spite of the sulphuric acid, however, a small quantity of these lower compounds is almost invariably present in guncotton.

Guncotton resembles ordinary cotton in appearance, but is somewhat harsher to the touch; in the compressed state it has a sp. gr. of about 1.0. It is insoluble in water, but dissolves in acetic ether (ethyl acetate) or nitrobenzene.

It can be exploded by percussion, but the detonation only extends to the portion actually struck. Damp guncotton when sufficiently washed is a very safe substance, for, on the application of a flame, it only burns quietly away as fast as it dries. If inflamed in air it unites with the oxygen and burns with a large white or yellow flame—

$$\underset{\text{Guncotton.}}{4\,C_6H_7O_2(NO_3)_3} + \underset{\text{Oxygen.}}{9\,O_2} = \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{24\,CO_2} + \underset{\text{Water.}}{14\,H_2O} + \underset{\substack{\text{Nitro-}\\\text{gen.}}}{6\,N_2}.$$

It is, however, highly sensitive to the shock produced by the explosion of a small quantity of fulminate of mercury, and then undergoes decomposition with great violence. The equation often given as representing the changes produced by its detonation is—

$$\underset{\text{Guncotton.}}{C_6H_7O_2(NO_3)_3} = \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{5CO} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{7CO_2} + \underset{\text{Hydrogen.}}{4H_2} + \underset{\text{Water.}}{3H_2O} + \underset{\substack{\text{Nitro-}\\\text{gen.}}}{3N_2}.$$

This equation does not really represent the composition of the gases set free on explosion. Actual analyses always show a larger volume of carbon monoxide than of the dioxide (generally about twice as much) and in addition there are sometimes hydrocarbons like acetylene and marsh-gas produced.

When guncotton undergoes detonation, the rapidity with which inflammation spreads is astonishing. It was determined by Sir F. Abel and found to be from 16,000 to 20,000 feet per second. One gramme of guncotton on detonation yields about 1000 thermal units and 700 cc. of permanent gases. (Cp. gunpowder, page 136.) The temperature of the explosion is estimated at 4000° C.

Guncotton is largely used for military purposes, the main mass of it being kept in a moist state so as to be practically uninflammable. It is detonated when wanted by means of a primer of dry guncotton, which is easily exploded by the aid of fulminate of mercury. Since the gases resulting from its decomposition contain several combustible ingredients, attempts have been made to increase the efficiency of guncotton by utilising this fact. Oxidising agents, like saltpetre or other nitrates, are therefore mixed with guncotton. Such mixtures are known under various names, *e.g.*—

POTENTITE, a mixture of guncotton with saltpetre.

TONITE, largely used in rock blasting, consists of about equal weights of guncotton and barium nitrate.

E. C. POWDER, used for sporting purposes, consists of a granulated mixture of guncotton and nitrates.

JOHNSON'S POWDER, also a granular mixture of soluble guncotton (soluble in alcohol and ether) with barium or potassium nitrate. In its manufacture camphor dissolved in petroleum ether is used; these are both distilled off (at about 100° C.).

Schultze's powder consists chiefly of "nitro-lignin," *i.e.,* grains of wood treated with a mixture of sulphuric and nitric acids, washed and dried; it often contains a small quantity of barium nitrate.

NITROGLYCERINE.

Nitroglycerine was discovered by Sobrero in 1841, but was not made on the large scale and used as an explosive until 1863, when its manufacture was commenced by Nobel, near Stockholm. Soon after its introduction several serious accidents occurred, which led to its prohibition by many governments. Nobel then introduced the use of dynamite, which permits of greater safety in carriage and use. Since then the manufacture of various kinds of nitroglycerine explosives has been carried on in steadily increasing quantities.

Nitroglycerine is prepared by the action of a mixture of strong sulphuric and nitric acids upon glycerine. In carrying out the process the greatest care has to be taken in order to avoid a rise of temperature, and the works are always erected in some out-of-the-way locality, so that in the event of an explosion the destruction shall be confined to the works themselves. The buildings generally consist of light wooden sheds surrounded with earth banks 25-30 feet in thickness; the walls and roof are lined with straw and the temperature is kept as constant as possible by means of water-pipes. The sheds are sometimes so sunk in the ground that the roofs only are visible; they are lighted by lamps placed outside; the floors are covered with fine sand, plaster of Paris or other absorbent mineral substance. The storehouses for the finished product are also usually below ground and some distance from the other sheds.

Large quantities are made at Ardeer, Scotland, by the Nobel Explosives Company.

The sulphuric acid used is the strongest oil of vitriol, sp. gr. 1.84; the nitric acid is usually made at the works and has a sp. gr. of 1.5. The glycerine is pure, of sp. gr. 1.26; it is obtained from candle- and soap-works. The acids are mixed in the proportion of 12 of nitric to 20 of sulphuric acid, and the mixture is thoroughly cooled by means of cold water flowing through leaden worms. The glycerine is then forced into the mixture of acids in the form of a spray, by compressed air, and the temperature of the whole carefully watched. By circulation of cold water through the leaden pipes and the regulation of the supply of glycerine the temperature is kept below 28° or 30° C. (about 85° F.). In many works an arrangement is provided by which, should a rise above this point occur, the whole contents of the leaden tank, acids and glycerine, may be discharged into a large tank half full of water, so that the charge is at once drowned and all risks of explosion avoided.

When the nitration is over, indicated by a fall in the thermometer, the charge is run into another leaden tank and allowed to stand for some time; the nitroglycerine gradually collects on the top of the acids, from which it is drawn off, thoroughly washed in a large quantity of water, then in a solution of sodium carbonate (in order to neutralise the last traces of acid), again with water, filtered through felt, and stored. Other methods, differing only in detail, are used for the preparation of nitroglycerine. In all cases the greatest precautions have to be taken in order to avoid rise of temperature. The presence of lower oxides of nitrogen in the nitric acid and leakage of water from the cooling worms are likely causes of overheating.

Nitroglycerine is an oily, colourless liquid of sp. gr.

1.6. Commercial specimens are often yellow or pale brown in colour. It has a sweetish and burning taste, and is poisonous, producing headache; 10 grains is a fatal dose. It is, however, used in small doses in medicine, in the treatment of certain heart diseases. It is almost insoluble in water, one gramme dissolving in about 800 cc., but is readily soluble in ether, chloroform, benzene, alcohol or nitric acid. When pure, it keeps indefinitely, but the presence of moisture or trace of free acid may cause its decomposition.

Its composition is expressed by the formula $C_3H_5(NO_3)_3$, being derived from glycerine, $C_3H_5(OH)_3$, by the replacement of the three OH groups by $(NO_3)_3$, and is thus similar in its constitution to guncotton $C_6H_7O_2(NO_3)_3$. It would therefore be better called *glyceryl tri-nitrate*.

It is volatile, without ebullition, at 100° C. (212° F.), and when heated to 180° or 200° C. (356°-392° F.) inflames or, sometimes, explodes. At low temperatures it becomes solid and melts at about 10° C. (50° F.).

It is somewhat difficult to set fire to nitroglycerine by a direct flame; in small quantities, it can be made to burn quietly, with a yellow flame, but if the quantity be large, there is usually a detonation. Detonation can be brought about by the shock of any other explosive, *e.g.*, fulminate of mercury.

The change produced in its explosion is thus represented—

$$\underset{\text{Nitroglycerine.}}{2\,C_3H_5(NO_3)_3} = \underset{\text{Carbon dioxide.}}{6\,CO_2} + \underset{\text{Water.}}{5\,H_2O} + \underset{\text{Nitrogen.}}{3\,N_2} + \underset{\text{Oxygen.}}{O.}$$

The volume of permanent gases evolved by one gramme of nitroglycerine is found to be 465 cc. at 0° C., and the quantity of heat, 1600 calories. The velocity of detonation is estimated at 5300 feet per second.

Nitroglycerine alone is not used at all in this country; indeed, its sale and transport are prohibited by law, but it is still employed to some extent in America. If it be absorbed in any indifferent, porous substance, it is rendered much less liable to accidental detonation. Such mixtures are called "dynamites."

KIESELGUHR DYNAMITE is the form in which nitroglycerine is most generally used. Kieselguhr, a bulky, siliceous earth, containing about 95-98% of silica and having a sp. gr. of 0.21, is calcined and mixed with three times its weight of nitroglycerine. The pasty mixture is then made into cartridges. The properties of dynamite resemble those of nitroglycerine, but it is less sensitive to shock and, being a solid, is more easily manipulated. Water expels the nitroglycerine from dynamite.

The velocity of propagation of the explosion in dynamite is found to be about 20,000 feet per second, about four times as rapid as in nitroglycerine. Other indifferent absorbents have been used in the preparation of dynamite, *e.g.*, magnesia alba, mica powder and charcoal. This last substance yields *"carbodynamite,"* which is claimed to possess certain advantages over the siliceous variety, amongst others, that water does not displace the nitroglycerine.

The explosion of nitroglycerine is attended with the liberation of fully oxidised gases and free oxygen (see equation, page 142), that of guncotton, it will be remembered, of gases which are susceptible of further oxidation. A mixture of nitroglycerine and guncotton might therefore be expected to afford a more violent decomposition than either separately. This is found to be the case, and various modifications of such a mixture are in use.

Blasting gelatine consists of a mixture of about 93% of nitroglycerine and 7% of guncotton, or, rather, dinitro-cellulose, $C_6H_8(NO_2)_2O_5$. The mixture is made at a temperature of about 30-35° C. (86-95° F.) and forms a viscous, translucent, semi-solid substance which freezes about 2° C. (35.6° F.). The frozen material, unlike frozen dynamite, is more easily exploded than the unfrozen. Blasting gelatine requires a larger detonator to ensure its explosion than does dynamite, but the intensity of its explosion is 1½ times as great as that of Kieselguhr dynamite No. 1. It can be rendered still safer by mixing it with 3% or 4% of camphor.

Gelatine dynamite, made by Nobel's Explosives Company, consists of a mixture of blasting gelatine (containing 97.5% of nitroglycerine and 2.5% of nitrated cotton), 65%; wood meal, 8.4%; potassium nitrate, 26%, and a little soda. It is a buff, elastic solid. Gelignite is a similar preparation.

Forcite, giant powder, vulcan powder, atlas powder, hercules powder, lithofracteur and rendrock are similar mixtures used in the United States.

Cordite, now largely used in the British army, consists of a mixture of 58% nitroglycerine with 37% of guncotton (reduced to a pulp by means of acetone, which afterwards evaporates) and 5% of vaseline. The pulp is squeezed through small holes into threads, which are placed in cartridges. The acetone vapour is very inflammable, and extra precautions on this account are necessary in the manufacturing process. (See p. 198.)

Many other explosives are in use, but can only have very brief mention here. Nearly all are, or contain nitro-compounds, *i.e.*, they are in many respects like guncotton or nitroglycerine. Many of them consist of a mixture of two or more substances, which alone are not explosive, and the mixture can be conveniently made immediately before use. Some, *e.g.*, Roburite, Securite and Bellite, have the great advantage of exploding without flame, so that they may be fired in atmospheres of explosive character (for example, that in a coal-mine) without danger of firing the gases.

Roburite consists of a mixture of mono-chlor-dinitrobenzene and ammonium nitrate; its decomposition is thus represented—

$$\underset{\text{chlordinitrobenzene.}}{C_6H_3Cl(NO_2)_2} + \underset{\text{ammonium nitrate.}}{9\,NH_4NO_3} =$$

$$6\,CO_2 + \underset{\text{Water.}}{19\,H_2O} + \underset{\text{Nitrogen.}}{10\,N_2} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

Both the ingredients are solid and the mixture is yellowish in colour and granular in structure. It is almost impossible to explode it by percussion or contact with a flame, but when exploded by a detonator it gives a violent effect equal to that of dynamite.

Bellite and securite are similar bodies, containing dinitrobenzene, $C_6H_4(NO_2)_2$, and ammonium nitrate, NH_4NO_3, or potassium nitrate, KNO_3.

Carbonite consists of nitrobenzene, $C_6H_5NO_2$ (a liquid), potassium nitrate and sulphur, mixed with kieselguhr.

Faviers' explosive is made by coating crystals of ammonium nitrate or sodium nitrate with a molten hydrocarbon, like paraffine, or with resin or nitronaphthalene.

Rackarock consists of 79% of potassium chlorate and 21% of nitrobenzene. The reaction on explosion is—

$$\underset{\text{Nitrobenzene.}}{6\,C_6H_5NO_2} + \underset{\text{Potassium chlorate.}}{25\,KClO_3} = \underset{\text{Potassium chloride.}}{25\,KCl} + \underset{\text{Carbon dioxide.}}{36\,CO_2} +$$

$$\underset{\text{Water.}}{15\,H_2O} + \underset{\text{Nitrogen.}}{3\,N_2.}$$

This explosive, which is slightly more powerful than dynamite, was used in immense quantities in the blasting of Flood Rock, Hell Gate, at the entrance to New York Harbour, in 1885.

KINETITE is a mixture containing 1% of guncotton, 20% of nitrobenzene, 80% of potassium chlorate or nitrate and 1-3% of antimony sulphide.

PICRIC ACID.—Another class of explosives contains, as the principal ingredient, *picric acid,* or tri-nitro-carbolic acid, $C_6H_2(NO_2)_3OH$. This substance alone, when properly detonated, is a powerful explosive. It melts at 120° C. (248° F.) and has a sp. gr. of 1.6 when cast. It is not easily exploded by shock or flame, unless it be mixed with certain oxides of metals, notably litharge, oxide of lead. Its salts, the picrates, are violently explosive. MELINITE and the recently introduced LYDDITE, used in the British army for shells, consist mainly of picric acid.

DETONATORS.—Fulminate of mercury, said to have the composition, $HgC_2N_2O_2$, is almost the only substance employed as a detonator. It is obtained by dissolving 1 part of mercury in 10 parts of nitric acid, sp. gr. 1.4, and mixing the solution with 8 parts of alcohol, sp. gr. 0.83. A reaction soon begins, after a time becomes violent, and on cooling, crystals of the fulminate separate and are filtered off.

Fulminate of mercury is a white, crystalline substance, almost insoluble in water, and of sp. gr. 4.4. When dry, or nearly dry, it explodes if struck or gently heated. Its temperature of ignition is between 150° C. and 200° C. (300°-392° F.), and it is estimated that the pressure produced by it in a space which it completely fills is twice as great as that produced by nitroglycerine. The decomposition is probably in accordance with the equation—

$$\underset{\text{Fulminate of mercury.}}{HgC_2N_2O_2} = \underset{\text{Mercury.}}{Hg} + \underset{\text{Carbon monoxide.}}{2\,CO} + \underset{\text{Nitrogen.}}{N_2}.$$

CHAPTER IX.

OILS.

" Fatty " and " Mineral " Oils—Characteristics of Fatty Oils in General—Testing Oils—Determination and Explanation of Specific Gravity, Viscosity, Oxygen Absorption, Free Acid, Saponification Value—Maumené's Test, Iodine Value—List of the more Important Animal and Vegetable Oils, giving, in Tabular Form, the above Constants and the Chief Uses—Petroleum and Its Products—Paraffine.

UNDER the term "oils" are classed numerous liquid or semi-solid substances of most diverse chemical composition and properties. The animal, vegetable and mineral kingdoms all furnish members, and consequently a rough division of the "oils" is founded on their origin.

The word oil is somewhat loosely used, being employed to designate any substance that possesses viscosity, so that such widely different compounds as sulphuric acid (oil of vitriol) and olive oil are, in common parlance, both spoken of as "oils." The chemist, on the contrary, restricts the term to those liquid or semi-solid substances which contain carbon, hydrogen and (generally) oxygen derived for the most part from natural sources.

The behaviour of oils on heating serves as a means of further classification; those which distil unchanged being called "volatile," while those which undergo decomposition or partial destruction are known as "fixed" oils.

The animal and vegetable oils are either fixed or volatile, while the mineral oils belong to the volatile group.

It is further customary to speak of the volatile animal and vegetable oils as "essential oils," and of the fixed oils as "fatty oils." As the latter group is the more important, it will be first considered.

THE FIXED OR FATTY OILS.

Besides the liquids there may be included in this group certain semi-solid or solid substances of animal or vegetable origin and of allied chemical composition, as spermaceti, tallow, palm oil, beeswax, carnauba wax.

The specific gravity of the liquids varies from .86 to .97, and of the solids from 0.87 to 0.99. Chemically, the liquid fatty oils are *glyceryl salts* of *certain organic acids,* known on account of their occurrence in oils as the *fatty acids.* The solid or semi-solid members and the *waxes* have a somewhat similar composition which it is not necessary, because of their lesser commercial importance, to enter into further.

In order that a clearer conception of what is meant by the expression "glyceryl salt of an organic acid" may be obtained, the behaviour of any typical fatty oil, such as olive oil, towards caustic soda is best studied.

Olive oil, when boiled with a solution of a caustic alkali, such as caustic soda, is split up into its components —glycerine (glycerol) and the fatty acid, which latter, however, immediately combines with the caustic soda to form a salt, sodium oleate—known under the general name of "soap."

By adding common salt to the solution obtained the soap is "salted out," *i.e.,* becomes insoluble and rises to the surface of the liquid, on cooling forming a solid cake. From the solution underneath glycerine may be obtained by evaporation and removal of the common salt, as a viscous, sweet-tasting, oily liquid, If the soap be dissolved in water and decomposed by the addition of dilute mineral acid, such as sulphuric, the fatty acid is set free from its combination with sodium and rises to the surface in oily drops.

From what has been stated above, it is evident that before a clear insight into the chemical nature of oils can be obtained the properties of both glycerine and the fatty acids must be studied.

GLYCERINE.—(Glycerol, sweet spirit of oils) $C_3H_5(OH)_3$.

Pure glycerine, such as the medicinal glycerine sold by the druggists, is a colourless viscid liquid of sweetish taste. It has a specific gravity of 1.27 and will mix with water in any proportion; in fact, it has a great attraction for this substance, absorbing it from the air; thus materials coated with or containing glycerine always keep moist and pliable. When heated, glycerine decomposes, giving rise to vapours of very penetrating odour, of which a familiar instance is the smell produced when a tallow candle or oil lamp (not a petroleum lamp) is blown out. These vapours consist of a decomposition product called *acrolein* ($CH_2 : CH.CHO$). Although glycerine cannot be distilled at the ordinary pressure, yet *in vacuo* or under greatly reduced pressure it boils undecomposed, and advantage is taken of this fact in the commercial preparation of glycerine from waste soap liquors.

Chemically, glycerine is a *trivalent alcohol, i.e.,* it is an alcohol capable of uniting with three chemical equivalents of an acid or with three molecules of a monobasic acid.

An alcohol in organic chemistry represents the hydrate or hydroxide of the metallic elements in inorganic chemistry, but the alcohols are much weaker in their properties than the inorganic hydrates or bases.

The monovalent organic alcohol, CH_3OH, is chemically analogous to sodium hydrate, NaOH. Glycol, $C_2H_4(OH)_2$, corresponds to calcium hydrate, $Ca(OH)_2$; glycerine, $C_3H_5(OH)_3$, has as its inorganic representative, bismuth hydrate, $Bi(OH)_3$.

Just as the three inorganic substances cited, when treated with, say, nitric acid, yield their corresponding nitrates, $NaNO_3$, $Ca(NO_3)_2$ and $Bi(NO_3)_3$, so the organic alcohols give the nitrates CH_3NO_3, $C_2H_4(NO_3)_2$ and $C_3H_5(NO_3)_3$ (nitroglycerine), respectively, and similar compounds (salts) may be obtained from these substances when other acids are employed, as, for example, acetic acid which yields methyl acetate, $CH_3C_2H_3O_2$.

In the case of hydrates and alcohols containing 2 or more groups, it is not essential that all the molecules of the acid which combine with one and the same molecule of the alcohol should be the same. By the union of dissimilar acidic molecules the so-called "mixed compound ethers" or "etherial salts" are produced, as, for example, glyceryl diaceto-nitrate, $C_3H_5(C_2H_3O_2)_2NO_3$. Reference to these mixed compounds will shortly be made.

Glycerine, besides its use in medicine and the toilet, is employed in the manufacture of nitroglycerine, for softening various substances, etc.

THE FATTY ACIDS are compounds of carbon, hydrogen and oxygen in varying proportions. Their acidic properties are much weaker than the acids of inorganic chemistry, being the strongest in the compounds containing the smallest proportions of carbon and hydrogen and decreasing in strength as the ratio of C and H to O increases. Like the inorganic acids, they react with the metallic hydroxides and alcohols to form salts, in which the metal or organic radical has been substituted for the replaceable hydrogen of the acid. Thus—

(a) $$\underset{\text{Acetic acid.}}{CH_3CO\,OH} + \underset{\substack{\text{Alcohol,}\\ \text{ethyl hydroxide.}}}{HOC_2H_5} = \underset{\text{Ethyl acetate.}}{CH_3COOC_2H_5} + \underset{\text{Water.}}{H_2O}.$$

(b) $$\underset{\text{Acetic acid.}}{CH_3CO\,OH} + \underset{\substack{\text{Sodium}\\ \text{hydroxide.}}}{HONa} = \underset{\text{Sodium acetate.}}{CH_3COONa} + \underset{\text{Water.}}{H_2O}.$$

(c) $$\underset{\text{Nitric acid.}}{NO_2OH} + \underset{\substack{\text{Sodium}\\ \text{hydroxide.}}}{HONa} = \underset{\substack{\text{Sodium}\\ \text{nitrate.}}}{NO_2ONa} + \underset{\text{Water.}}{H_2O}.$$

(d) $$\underset{\text{Nitric acid.}}{NO_2OH} + \underset{\substack{\text{Ethyl hydroxide,}\\ \text{or alcohol.}}}{HOC_2H_5} = \underset{\text{Ethyl nitrate.}}{NO_2OC_2H_5} + \underset{\text{Water.}}{H_2O}.$$

As already shown, the fatty acids are contained in the oils in the form of glyceryl salts, but it may be here pointed out that one and the same oil may contain many different fatty acids; thus from linseed oil the following acids have been obtained—linolenic, isolinolenic, linolic, oleic, stearic and palmitic.

According to the relationships of the quantities of carbon and hydrogen present in the molecule, the fatty acids have been classed in the following series or groups. Only the most important acids are given:

SATURATED ACIDS.

(a) *Acetic or Stearic Series.*—General formula, $C_nH_{2n+1}\,COOH$.

(1) Formic acid, H.COOH, in nettles, ants, bees, etc.

(2) Acetic acid, CH_3COOH, in vinegar.

(3) Butyric acid, C_3H_7COOH, in butter.

(4) Capric acid, $C_9H_{19}COOH$, in butter and cocoanut oil.

(5) Myristic acid, $C_{13}H_{27}COOH$, in spermaceti and cocoanut oil.

(6) Palmitic acid, $C_{16}H_{33}COOH$, in palm oil and many animal fats.

(7) Stearic acid, $C_{17}H_{35}COOH$, in tallows and many oils.

The simpler members of this series are liquids of penetrating odour, while the higher members, as palmitic and stearic acid, are, at the ordinary temperature, odourless, white solids.

UNSATURATED ACIDS.

(b) *Oleic Series,* $C_n H_{2n-1} COOH$.
   (1) Crotonic acid, C_3H_5COOH, in croton oil.
   (2) Oleic acid, $C_{17}H_{33}COOH$, in olive and other oils.
   (3) Brassic acid, $C_{21}H_{41}COOH$, in rape and colza oil.

(c) *Linolic or Linoleic Series,* $C_n H_{2n-3} COOH$.
   (1) Linolic acid, $C_{17}H_{31}COOH$, in linseed and other drying oils.
   (2) Ricinoleic acid, $C_{18}H_{32}(OH).COOH$, in castor oil.

(d) *Propiolic Acid Series,* $C_n H_{2n-5} COOH$.
   (1) Linolenic acid, $C_{17}H_{29}COOH$.
   (2) Isolinolenic acid, $C_{17}H_{29}COOH$.

Both occur in linseed and other drying oils.

Since glycerine is common to them all, evidently the characteristic behaviour of an oil depends on the nature of the fatty acids it contains. In the list just given the acids are divided into two groups, the saturated and unsaturated acids. The former are much the more stable, they are not easily attacked by oxidising agents, nor are they affected by reducing agents or exposure to air. On the other hand, the unsaturated acids are readily oxidised, becoming rancid or viscous when exposed to the action of atmospheric oxygen, combining with chlorine, bromine or iodine until they are saturated. This susceptibility to the action of external agencies increases as the acids become less saturated; thus linolenic acid absorbs oxygen more readily and in larger quantities than does oleic acid.

The terms *saturated* and *unsaturated* denote the relative amounts of H or other element or group of elements, called *radicals,* with which an atom of carbon is combined. Marsh-gas, CH_4, and ethane, C_2H_6, are saturated compounds, because the carbon is combined with all the hydrogen it can take up, but ethylene, C_2H_4, and acetylene, C_2H_2, are unsaturated because they are capable of uniting with two or four more atoms of hydrogen (or monovalent element) respectively.

In the oils, where more than one fatty acid is present, it is interesting to inquire if the various fatty acids exist combined separately with glycerine, or if they exist as mixed glyceryl salts. Thus, to take linseed oil containing, say, linolenic, linolic and oleic acids, do these acids exist in the oil as mixtures of glyceryl tri-linolenate, glyceryl tri-linolate and glyceryl trioleate,

$$C_3H_5(C_{18}H_{29}O_2)_3,\ \ C_3H_5(C_{18}H_{31}O_2)_3 \text{ and } C_3H_5(C_{18}H_{33}O_2)_3,$$

respectively, or are they present as glyceryl linoleno-linolo-oleate?

$$C_3H_5 \begin{cases} C_{18}H_{29}O_2 \\ C_{18}H_{31}O_2 \\ C_{18}H_{33}O_2. \end{cases}$$

For linseed oil this question has not been answered, but probably both views are correct, the acids existing partly, as in the latter, and partly, where there is an excess of any acid, as in the former case.

The chemical behaviour of oils depending on the nature of the fatty acids they contain, many of the methods in use for testing oils are based on the differences in properties which the acids show.

The most important tests for recognising and determining the suitability of oils used for lubrication, dressing, painting, etc., are briefly given below.

PHYSICAL TESTS.

Specific Gravity.—This constant is best determined by means of a specific gravity bottle. This is usually made to contain 10, 25 or 50 grammes of water at 15.5° C. (60° F.). In carrying out the experiment the bottle is weighed empty, then filled with water at 60° F. and again weighed, when, if accurately made, it should contain 10, 25 or 50 grammes, as the case may be. After drying it is filled with the oil to be tested, preferably at the same temperature, and again weighed.

$$\text{Specific Gravity} = \frac{\text{Weight of oil}}{\text{Weight of equal volume of water}}.$$

Specific Viscosity.—This is measured by observing the rate of flow of the oil through a narrow orifice or tube, at a certain temperature, and comparing it with the rate of flow of rape oil under exactly similar conditions. An ordinary burette filled to the same mark in two experiments with rape oil and the oil to be tested serves very well as a simple viscosimeter. The quantities of oil flowing in the same time give the relative viscosity, rape oil being usually taken as 100. For further details the reader is referred to Bendickt & Lewkowitsch, Oils, Fats and Waxes.

CHEMICAL TESTS.

Oxygen Absorption.—According to their power of absorbing oxygen from the air, oils are divided into two groups—*drying* and *non-drying*.

The drying oils, as linseed oil, absorb oxygen rapidly, changing into solid substances; the non-drying, neatsfoot, sperm, etc., show no marked tendency to do this, becoming, however, in some cases rancid and slightly more viscous. Midway between the two classes stands a number of oils, such as cottonseed, rape, etc., known as the *semi-drying oils*. Livache determines the amount of oxygen which an oil will absorb by spreading it over a porous material, as precipitated lead, and observing the increase in weight on exposure to air after the lapse of several days. M. Weger recommends that the oil be spread as thin as possible on weighed glass plates and the changes in weight noted at regular intervals. By the above methods it is found that—

	Per cent.		
	(Livache).		(Weger).
Raw linseed oil gains......	14.3		17.2-19.9
Boiled linseed oil gains....	..		13.3-17.6
Cottonseed oil gains.....	5.9	in 2 days	
Rape and colza oil gain...	2.9	“ 7 “	
Olive oil gains..........	1.7	“ 7 “	
Whale oil gains.........	8.26	“ 3 “	
Cod liver oil gains.......	6.4	“ 3 “	
Sperm oil gains.........	1.6	“ 3 “	

As the absorption of oxygen is brought about by actual chemical union between the oil and oxygen, and so produces heat, this test is of value in determining the danger of spontaneous combustion in using an oil.

Maumené Test.—Oils, when mixed with concentrated sulphuric acid, show a considerable rise in temperature. This increase is greater with the drying oils than with the non-drying, and has been used as a method for their recognition. A weighed quantity of oil (say 50 grammes) is placed in a small glass vessel resting in a box filled with cotton wool and its temperature accurately noted. A known quantity of concentrated sulphuric acid (say 10 cc.) at the same temperature is gradually added, and, the thermometer being used as a stirrer, the rise in temperature carefully observed. This temperature increase, provided that the experiment is always carried out in the same manner, is constant for the same oil. (The results obtained with standard oils are given in the table, p. 158.)

Free Acid or Acid Value of Oils.—The quantity of free acid present in an oil—a very important factor in judging its suitability for lubrication and for cloth oils, etc.—is estimated by measuring the quantity of a solution of caustic potash or soda of known strength that is required to neutralise a given weight of the oil, *i.e.*, to completely saturate the free fatty acids present. Some oils contain large amounts of free acids, as, for example, palm oil, which is met with in commerce containing as much as 80% free palmitic acid.

Saponification Value and Unsaponifiable Matter.—As already stated, when an oil is boiled with a solution of caustic soda it is decomposed into glycerin and the fatty acid or acids it may contain, which latter combine with the alkali to form a soap. By taking a weighed quantity of oil and a weighed quantity of alkali (which must be in excess) it is possible by chemical means to determine the amount of alkali used to decompose the oil and to form soaps with the fatty acids present; this quantity is calculated to milligrammes of caustic potash (KOH) required per gramme of oil and is known as its *saponification value.* Thus 1 gramme of linseed oil requires for saponification 193 milligrammes of caustic potash (KOH); therefore 193 is the saponification value of linseed oil; rape oil, on the other hand, has a saponification value of 177.

It should be noted that the saponification value depends on the molecular weight of the fatty acids present in the oil, being higher with those of low molecular weight and lower as the molecular weight of the acids increases.

In carrying out the determination of the saponification value any substance that is not decomposed by alkali will remain unaltered in the solution and may be removed therefrom by means of ether or other suitable solvent. After evaporation of the ether this remains, if non-volatile, as a residue which may be weighed, and so the quantity of "unsaponifiable matter," *i.e.*, substances which will not form soaps with alkali, may be determined.

Mineral oils, rosin oil and the hydrocarbons generally are not saponifiable; hence the presence of a large quantity of unsaponifiable matter* in a commercial oil points to these substances. (See also Cloth Oils, page 182.)

Iodine Value.—Hübl has shown that when an oil is treated with an alcoholic solution of iodine containing mercuric chloride, the quantity of iodine absorbed is greater with the drying oils than with the non-drying.

The "iodine value" of an oil is the percentage of iodine which it will absorb in this way. Detail of the method would be out of place here, and references must be made to some standard work on oils.

The iodine is absorbed by the unsaturated acids and

---

* A ready test for unsaponifiable matter is to dissolve a small piece of caustic potash or soda in absolute alcohol, add to the solution a few drops of the oil and boil until it clarifies. This solution is added to distilled water; if a cloudiness is produced unsaponifiable matter is present.

OIL OR FAT.	SOURCE.	SPECIFIC GRAVITY.	SAPONIFICATION VALUE.	IODINE VALUE.	MAUMENÉ TEST.	USES AND REMARKS.
Tallow, Beef	Oxen	0.934–0.952	193–200	35.4	31.6 C	Lubricant, Soaps, Candles.
Lard	Pigs	0.931–0.938	196	50–60	13–30	As Food.
Neatsfoot	Calves	0.914–0.916	194	69–70	47–51	Lubricant, Leather Dressing.
Whale or Train.	"Blubber"	0.925–0.930	188–193	101	61–92	Burning and Leather dressing.
Seal	Seals	0.915–0.926	178–196	125–152	92	Leather dressing.
Cod Liver	Codfish	0.922–0.927	171–213	123–152	102–106	Leather dressing and in Medicine.
Sperm	Sperm Whale.	0.875–0.880	123–147	81–84	45–51	Lubricant.
Olive	Olives	0.917–0.918	188–196	77–86	35–45	Foods, Soaps, Burning, Dyeing.
Cottonseed	Cotton	0.916–0.923	191–196	102–108	74–90	Adulterant of other oils, Soaps, Food, Blown oils, etc.
Rape and Colza.	Plants	0.911–0.917	170–176	98–105	55–64	Burning and Lubrication.
Maize or Corn	Maize	0.921–0.924	188–193	111–122	56–89	Adulterant, Burning and Lubrication, Soaps.
Castor	Seed	0.960–0.967	176–183	83–85	47	Soaps, Medicine, "Turkey Red Oils."
Linseed	Flax	0.932–0.935	187–195	166–187	104–124	Paints, Varnishes, Linoleum, Soaps.
Tung	Oil Tree	0.934–0.938	192–194	166		Varnishes (very powerful drying oil)

Oils with an Iodine value above 100 are regarded as *semi-drying* oils, while those with Iodine values above 150 are looked upon as *drying* oils.

hence this value affords us a useful means of comparing the drying powers of oils. The numbers obtained do not in all cases agree with those calculated from the oxygen absorption, although a certain amount of proportionality does exist. The reasons for these differences are but little understood, although they are partly explained by the fact that in carrying out the determination of the iodine value it is almost impossible to avoid substitution* taking place as well as the addition of iodine.

Still, as the results obtained are constant with the same oil, if carefully performed a determination of the iodine value forms one of the surest and readiest means of identifying an oil and of judging its suitability for lubrication or painting and the dangers of spontaneous combustion which may attend its use. (See table.)

EXTRACTION OF OILS.

Animal and Fish Oils.—These oils are usually extracted by boiling the raw material with water when the oil swims on the surface and is run off from the aqueous portion below. After filtering, the crude oil is generally refined either by freezing, or by treatment with a small quantity of dilute alkali or with sulphuric acid and bichromate of potash. In some cases the raw material is first rendered at a steam heat, the oil filtered from the membranous residue and then treated with boiling water. Sometimes the crude substance is allowed to partly putrefy (as in the case of liver oils and bone oils); when the oil exudes of itself, it is drained away, filtered and washed.

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* By "substitution" is meant the replacement of some of the hydrogen atoms in the molecule of a carbon compound by iodine or other element. By "addition" is meant the adding on of iodine or other element to an unsaturated compound, so that it becomes more or entirely saturated. The ideal iodine value is based upon a determination of the added iodine only.

The putrescent residue is then boiled with water, when a further quantity of oil is obtained.

There are, in addition to those methods mentioned, special modes of procedure applicable to special oils, but these hardly come within the scope of this work.

VEGETABLE FATTY OILS.—Three chief methods of extraction are in use—

(a) Pressure; the most commonly employed method.
(b) Extraction by volatile solvents.
(c) Boiling the bruised seed or fruit with water.

Previous to extraction of the oil the seeds are cleaned, decorticated (*i.e.,* removed from their shells), crushed and ground by passage through specially constructed rollers or mills, and often gently heated, in order to coagulate the albumen and liberate the oil.

(a) *Pressure Extraction.*—The crushed and moistened seed is placed either in bags (often of horse hair) or in moulds, and subjected to hydraulic pressure, first in the cold ("cold drawn oil") and then under heat ("hot drawn").

The accompanying diagram represents a press for seeds on the American system (Fig. 38).

After extraction the oil is generally refined by heating in a tank by steam-pipes to 160-170° C. (320-338° F.) and sometimes by treatment with sulphuric acid or a small quantity of caustic soda. It is then tanked until required. The residue left in the moulds or bags still contains some oil (6-15%) and is used as a food for cattle (cotton and linseed cake).

(b) *Extraction by Solvents.*—The crushed seeds in bags or cages are placed in iron cylinders arranged in series. Here they are subjected to the solvent action of such substances as petroleum naphtha or carbon disulphide which are forced through the cylinders, the whole process being similar to the lixiviation of black ash in the manufacture of soda.

From the solution thus obtained the oil is recovered by distilling off the solvent and is refined as before. By this process an increased yield of oil is obtained, but if not very carefully conducted there is considerable risk of fire, the volatile solvent being extremely inflammable, and the process has also the disadvantage that the residue

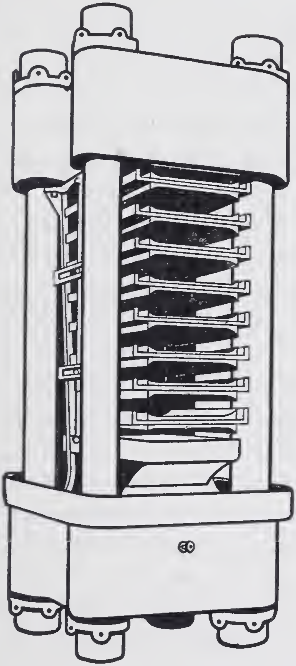

FIG. 38.—Oil Press.

of seeds left is much less valuable, as it usually contains little oil. The oil, too, obtained by this method is of inferior quality.

(c) *Extraction by Boiling with Water.*—Castor oil is extracted by the natives of the countries where it is grown by a process similar to that adopted with animal and fish oil. Some olive oil is also made by this method.

MINERAL OILS.

The most important sources of these substances are the petroleum springs of America, Caucasus, Galicia, etc., and the oil shales found in Scotland and elsewhere.

No matter of what origin, mineral oils are chemically hydrocarbons, that is, compounds of carbon with hydrogen in different proportions, and they contain, when pure, no oxygen, in which they are distinguished from fatty oils.

Marsh-gas or methane, CH_4; ethylene, C_2H_4, and acetylene, C_2H_2, have already been mentioned and some of their properties studied.

The mineral oils are mixtures of similar hydrocarbons, which may be classed in the following groups—

(1) The Methane or Paraffin Series, C_nH_{2n+2}. Members of this series are present in all the mineral oils, American petroleum being the richest in them.

(2) Ethylene or Olefine Series, C_nH_{2n}. Olefines occur in shale oils and are present to some extent in Russian oil.

(3) Acetylene Series, C_nH_{2n-2}. Members of this series have not been detected with certainty in mineral oil.

(4) The Naphthenes, C_nH_{2n}. Russian petroleum consists very largely of hydrocarbons, which, on account of their properties, are classed under a different series,

namely, the naphthenes, C_nH_{2n}, not in any way similar to the olefines. They react, in fact, like saturated compounds.

(5) The Benzene Series, C_nH_{2n-6}. Members of this series are found in many shale products.

General Properties of Hydrocarbons.—It will be understood from what has already been said that the properties of the hydrocarbons present in oils are in many ways similar to the gaseous hydrocarbons already mentioned. They are all easily combustible, burning in air to form carbon dioxide and water.

The paraffins are less susceptible to the action of chemical agencies than the olefines and the olefines less than the acetylenes.

The molecular weight of the various hydrocarbons increases with the boiling and melting points. Thus, the lower boiling fractions of American oil, as cymogene (see below), contain such hydrocarbons as propane, C_3H_8; butane, C_4H_{10}; pentane, C_5H_{12}; hexylene, C_6H_{12}, etc., while the higher boiling portions contain hydrocarbons of the formulæ $C_{20}H_{42}$, $C_{18}H_{38}$, etc., and are solids.

Petroleum.—Is a natural product found in many parts of the world, notably in America, Caucasus, Galicia, India, etc., which probably owes its origin to the combined action of subterranean heat and pressure on fish remains, and so is indirectly of animal origin.

The crude oil, usually accompanied by gaseous hydrocarbons, issues from conglomerate strata, which in America are situated between shale beds. These strata are tapped by borings from which the oil is conveyed in pipes to the refineries, where it is distilled and separated into various "fractions" according to the boiling points and specific gravities.

American Method of Refining.—The stills used are of two kinds; while the naphtha and burning oil are "run" from one still, the residuum is treated in a separate still called a "tar still" to obtain from it the higher boiling fractions, the light and heavy lubricating oils, vaseline and paraffin wax.

The naphtha or benzine, as it is called, forms 12% of the crude American oil, and on being redistilled is separated into the following portions:

Cymogene.—Boils at 0° C. (32° F.), is gaseous at the ordinary temperature and is employed in ice making. This substance is very inflammable.

Petroleum Ether.—Boils at 70-90° C. (158-194° F.). Sp. gr. 0.656-0.666, used as a solvent for india-rubber and oils. Also called Sherwood's oil.

Gasoline.—Another form of the last is largely used for extracting oils from seeds, etc. The above three substances form 25% of the benzine.

Naphtha (Danforth's oil).—Boiling from 80-110° C. (176-230° F.), and having a specific gravity of 0.69-0.70, forms another 25%, and is used for burning in vapour stoves and in street lamps or "flares," as a solvent for resins in varnish making and in oilcloth manufacture.

Ligroin.—Boiling point 80-120° C. (176-248° F.); sp. gr. 0.710-0.730; is used in sponge lamps, as solvent for gums, waxes and resins and for cleaning.

Benzine or Benzoline.—Boiling point 120-130° C. (230-248° F.); sp. gr. 0.730-0.750; forms about 40% of the distillate. It is deodorised by treatment with sulphuric acid and then employed as a turpentine substitute.

All the above substances "flash" at the ordinary temperature.

After the naphtha has been run from the stills the burning oils distil over. They are known under the name of *kerosene* or *petroleum.* This forms 35-50% of the crude oil, or in some cases where the oils are "cracked" as much as 80%. Enormous quantities are distilled in America (523 millions of gallons in 1890). It is refined by treatment with sulphuric acid and caustic soda.

Kerosene, petroleum, or, as it is wrongly called, *paraffin,* is a limpid liquid of more or less unpleasant odour. It boils between 150-300° C. (302-572° F.) and has a specific gravity of 0.79-0.80. Its chief use is in lamps. (See chapter on illuminants.)

The dangers attending the use of petroleum are so important that they will be considered at some length. It may be safely employed in lamps, provided that the temperature of the oil reservoir never under normal conditions rises above the point at which the petroleum contained therein evolves sufficient vapour to form an explosive mixture with air ("flash-point"). In a properly constructed lamp, the highest temperature attained by the oil in the body should, even after long-continued use, be several degrees below the legal flash-point.

In testing an oil for its flashing temperature the most rational method would be to heat the petroleum to a given temperature, shake it well with air and apply a flame to the mixture, noticing if an explosion occurs. Although this would appear a simple method, yet the legal test for petroleum is carried out with an apparatus in which insufficient care is taken to insure proper admixture of the vapour with air.

In this country and in Germany the official apparatus is that of Abel; it consists essentially of a closed chamber containing the petroleum and surrounded by a water bath (Fig. 39). By means of a delicate thermometer inserted in the oil its temperature may be observed, and as it rises 0.5° a small flame is lowered through an opening in the lid and removed. The process is repeated until a "flash" or slight explosion is noted, and the temperature then indicated by the thermometer is called the "flash-point."

The minimum "flash-point" permissible for a petroleum for use in lamps is, at present, 73° F. in this country.

The great number of accidents arising from petroleum led the British Government to appoint a Select Committee of the House of Commons to consider the law relating to the sale, etc., of petroleum and the precautions to be adopted with petroleum lamps. The sittings having extended over four sessions and much expert evidence having been heard, in July, 1898, the Committee issued their report, in which it is recommended, among other things—

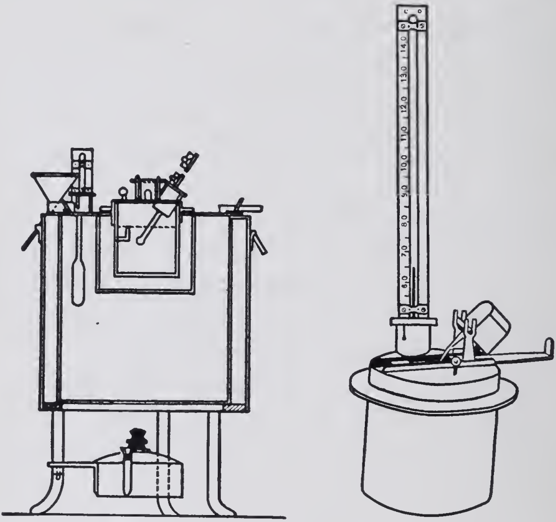

Fig. 39.—Flash-Point Apparatus. On the left of the figure is an enlarged view of the oil-cup, showing the thermometer and the small tilting lamp, by which the flame can be brought to the mixture of vapour and air in the cup.

(1) That the legal flash-point for petroleum oil be raised to 100° F. (Abel's closed test).

(2) That the laws relating to the sale, storage, etc., of petroleum oil and spirit and the manufacture of lamps be amended.

(3) That inquiries be made into the causes of accidents and adequate supervision and administration of the law by local authorities be provided.

These recommendations are undoubtedly excellent;* 73° F. is a temperature often attained, even in this country in the summer months, and great danger must attend the handling of any liquid which is (at the temperature stated) giving off inflammable vapour.

Higher temperatures are met with in shops and on board ship, care must therefore be taken not to approach any vessel containing petroleum with a naked flame.

The raising of the flash-points will necessitate the removal of some of the lower boiling constituents from the oil, and it is also stated that some of the higher boiling constituents will have to be removed. There is little or no demand for these substances, so it is feared that the cost of production of a higher flashing oil, such as is recommended by the Committee, would be so materially increased as to render its price prohibitive. A writer in a continental trade journal states that a crude Russian oil

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* The "Petroleum Bill," the main objects of which were to raise the legal flash-point of commercial petroleum oil to 100° F. (37.70° C.) and to substitute the Abel closed test for the "open" test came before the House of Commons on March 15, 1899, for its second reading, and was rejected by 244 to 159. In the course of the discussion it was alleged that the bill was really a protective measure intended to benefit the Scotch paraffin industry and the owners of the Russian oil wells at the expense of the American producers. The supporters of the bills pointed out that 105° F. was the flash-point insisted upon for military and naval purposes, while for light-houses 120° or 150° F. was demanded. In the State of Iowa the legal flash-point was 105°, and it was said that not a single death from petroleum explosion had occurred there for the last fourteen years, while in London (with double the population) there had been 191 deaths during the same period. It was stated that the Government had in prospect a bill to regulate the manufacture and enforce improvements in paraffin lamps.

yielding 33% of low-flashing kerosene would only furnish 15-16% of the high-flashing product (40° C. or 105° F.), the remaining 17-18% being practically useless.*

As already mentioned, after the burning oils have distilled over, the residue is transferred to the tar stills and the distillation carried further. Above 300° C. (572° F.) the distillate of dark colour and greater density is received in the "paraffin agitator," where it is refined by treatment with sulphuric acid and dilute caustic soda solution, then it is run into the "chilling room" and the paraffin wax frozen out.

By filtering under pressure through bags "paraffin scale" is obtained, and the liquid portions are used as mineral lubricating oils.

If the distillation is conducted under reduced pressure, "vaseline," used for making salves and ointments and so largely for greasing iron to prevent rust, is produced.

Paraffin Scale.—As obtained from the press cake, the scale is very impure, containing much heavy mineral oils. The latter is removed by the "sweating" process, which consists in gradually raising the temperature of the mass placed on perforated plates so that the more easily fusible materials may run away. Further purification by melting to settle out the dirt, hydraulic pressure and washing with naphtha follows.

When pure, paraffin wax or "paraffin" is a white, waxy substance without odour or taste, which melts at 45-80° C. (113-194° F.), and has a specific gravity of 0.869-0.943. It is largely used in making candles, in water-proofing textiles, for preserving wood, for "pitching" brewers' casks, for dipping matches, in the manufacture of insulating materials for electrical purposes, etc.

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* Dr. S. Strausky, *Chem. Rev. Harz und Fett. Industrie*, Dec., 1898, p. 229.

Caucasian Petroleum.—As already intimated, these oils contain hydrocarbons which belong to a different class to those present in American oils, namely, the naphthenes (about 80%). In the distillation of the Caucasian oils, the chief object is not, as with American petroleum, to obtain burning oil, because the heavier portions yield most excellent lubricating oils, hence the "cracking" method is not often adopted. Otherwise the treatment and the products are very similar save that in the fractions boiling at the same temperature in both, the Caucasian oils are invariably heavier. Thus—

Fraction.	Specific gravity.	
	Baku oil.	American.
140-160° C.	0.782	0.755
190-210° C.	0.820	0.786
240-260° C.	0.845	0.812

Much less naphtha and burning oil are consequently obtained and more of the heavier oils. The residue left in the stills, "astaki," or "massud" as it is called, is largely used on the spot as fuel for locomotive and steamer engines. (See Chap. V., p. 74.)

Shale Oils.—In Scotland and also in some parts of Germany mineral oils, including naphtha, burning oil, lubricating oils and paraffin wax, are obtained by a process invented by James Young, in 1851, from carbonaceous or bituminous shales. On distillation these "oil shales" yield a green, oily liquid and a weak ammoniacal liquor. The crude oil is separated and dehydrated when it shows a specific gravity of 0.880-0.890 and solidifies at the ordinary temperature.

By repeated redistillation and treatments with sulphuric acid (to remove amines and alkaloids, as aniline and pyridine, etc.) and caustic soda (to remove phenols) the following products are obtained therefrom:

Shale spirit or naphtha........	Sp. gr.	0.700-0.740
Burning or paraffin oil........	“	0.800-0.820
Medium or light mineral oil....	“	0.840-0.865
Heavy lubricating oil..........	“	0.875-0.895
Paraffin scale or wax..........	M. P.	86-140° F.

And from the alkaline washing, phenol or carbolic acid and creasote.

Generally speaking, the flash-point of the shale products is higher than that of the corresponding American ones.

GALICIAN PETROLEUM.—Similar to the Caucasian, is but little used in this country, as is also the German shale oil.

RANGOON TAR.—Also furnishes a number of petroleum products.

CHAPTER X.

TECHNICAL APPLICATIONS OF OILS.

Oils for Lubrication—In Leather Industries—In Cloth Manufactures—"Oleine"—"Yorkshire Grease"—"Recovered Oils"—"Seak Oil"—"Black Oils"—Oils in Dyeing—"Turkey Red" Processes.

OILS AS LUBRICANTS.

To be a good and safe lubricant an oil must, according to Benedikt & Lewkowitsch, fulfil the following conditions:

(1) It should diminish friction.

(2) Should not lose its lubricating property on exposure to the atmosphere (*i.e.,* should not "gum").

(3) Should have no deleterious action on the bearings or metallic surfaces with which it comes in contact.

(4) Should possess a sufficient degree of viscosity, so that it is neither squeezed out from between the moving surfaces nor wasted by the motion of the machinery.

(5) Should not give off combustible gases or vapours at the temperature to which it is heated when in use.

It is obvious that one and the same oil cannot be expected to fulfil all the above conditions under the varying temperatures, speeds, loads and other influences to which various bearings are exposed.

Consequently it is very important to make the right choice of an oil for use as a lubricant, and it is, therefore, proposed to briefly indicate those oils which are employed, the purposes for which they are used and what advantages or disadvantages they severally possess.

Representatives of all the classes of oils find application as lubricants, namely, animal and vegetable fatty oils, etc., and mineral oils.

Following the plan already adopted, the fatty oils will be first considered.

FATTY OILS.—The most commonly used fatty oils are:

(1) *Sperm Oil.*—On account of its comparatively low viscosity, which, however, it retains with little loss, even at high temperatures, this oil finds considerable use for quick-running machinery, as spindles, but, unfortunately, it is rather expensive.

(2) *Neatsfoot Oil* greatly loses in viscosity when heated, and is consequently only employed for such bearings as are exposed to comparatively low temperatures. As it usually contains but little free fatty acid, and does not easily become rancid or gum, neatsfoot oil is used for machinery where corrosion through chemical action must be especially avoided.

(3) *Lard Oil and Tallow Oil* are, like neatsfoot oil, very susceptible to changes in temperature, but as they exhibit no tendency to become rancid or gum, they are employed as lubricants for shafting, and engine and machinery bearings generally.

(4) *Castor Oil,* distinguished by its great viscosity, which it loses, however, with increase of temperature, is used for heavy bearings.

(5) *Olive Oil,* though apt to become rancid and to contain free acid, is, on account of its great viscosity, employed for bearings running at high speeds which have to carry moderately heavy loads.

(6) *Rape and Colza Oil* have also found favour as lubricants. They have high viscosity, but, unfortunately,

show a tendency to gum. They are chiefly employed for engine bearings and cylinders.

(7) *Tallow* is used for heavy loads at high temperature, as in cylinders.

It may be here stated that no fatty oil is suitable for cylinder lubrication, since, under the action of high-pressure steam, they are split up, yielding free fatty acids, which corrode the interior of the cylinder and, by finding their way into the condenser water and thence into the boilers, produce therein a very objectionable scale. Neither should any drying or semi-drying oil be used as a lubricant, for by exposure to the air they oxidise or "gum" and clog the bearings.

MINERAL OILS.—These lubricants, of comparatively recent introduction, are rapidly replacing the fatty oils in the arts.

They are the higher boiling portions of petroleum and shale oil, consisting essentially of mixtures of hydrocarbons and varying in viscosity and gravity from thin spindle oil of a light yellow to dark, thick cylinder oils and semi-solid greases. Hydrocarbon oils have several disadvantages attending their use; they lose much of their viscosity with increase of temperature, and if not carefully prepared they are apt to give off inflammable vapours, whereby their use may involve greater danger of fire.

On the other hand, a carefully prepared mineral oil of high flash-point is an excellent lubricant; it does not gum or become rancid and exerts no action on the metallic surfaces.

OPEN TEST.—Before any oil can be considered a safe lubricant it should be examined for its flash-point. This is usually done by what is known as the "Open Test" method. About 50 c.c. (2 oz.) of the oil are heated in a porcelain basin or glass beaker placed in a sand bath and stirred by a thermometer; from time to time, every 5° C. (9° F.) rise in temperature, a small flame is brought near the surface of the oil. The temperature indicated by the thermometer when a "flash" or slight explosion is observed is taken and called the "flash-point" of the oil. The heating is continued further, and the flame repeatedly applied, until the oil begins to burn steadily in the basin, when the temperature is again read off, giving the "Fire Point."

CLOSED TEST.—This is carried out for the railway companies in America in an apparatus known as Elliott's beaker, and is applied chiefly to burning oils of high flash-point, rarely to lubricating oils. The Elliott apparatus resembles Abel's, but instead of heating by a water bath the oil is supported in the beaker some distance above the flame of a small petroleum lamp, the heating power of which can be regulated by manipulation of the wick. The oil in the beaker is covered by a glass plate, through which the thermometer passes, and has an opening to allow of the introduction of a flame. The procedure is the same as with the open test.

No oil should be used for lubricating bearings, etc., which has a lower flash-point than 140° C. (284° F.), nor for cylinder lubrication which flashes below 180° C. (356° F.) (open test).

For railway carriage axle lubrication 160° C. (320° F.) is the flash-point recommended by the Deutscher Verband für die Material-prüfung der Technik. It is also considered that a mineral oil should not lose more than 1 per cent. of its weight by heating for 6 hours at the maximum temperature to which it will be exposed in practice.

Fatty oils usually flash at 200-260° C. (392-500° F.), and so they may be employed for lubrication without danger. On the other hand, mineral oils, especially if they contain water or a trace of the low boiling petroleum or shale products, flash at a much lower temperature. A half per cent. of benzine added to a mineral oil flashing at 186° C. (367° F.) depressed the flash-point 80° C. (172° F.) (closed test) while in the open test, owing to the quick evaporation of the benzine, no depression was observed. Carefully prepared mineral oils can be obtained of almost any flash-point, so the above remarks are made only with reference to the cheap, unrefined oils which are sometimes offered for sale. Before purchasing such products the consumer is recommended to have them examined for their flash-points.

Mixed Oils.—The loss of viscosity, which most mineral oils suffer with increase of temperature, is corrected in many commercial lubricants by adding to them a certain proportion of some fatty oil. Such mixtures combine, in some measure, the good qualities of both; they gum less readily and do not attack the bearings so much as the fatty oils when used alone; but as they are generally sold under fancy names and at fancy prices, it is best for the consumer to make his own mixtures. Many of the "Valvolines" and cylinder oils intended to work under heavy pressures are such mixtures of mineral oil with tallow; they are but little suited for that purpose (see fatty oils), although the decomposition of the fatty oil by the high-pressure steam is partly prevented by the presence of the mineral oil.

Castor oil (dissolved in lard oil) and blown rape or cottonseed oil are also used as admixtures with mineral oil to increase its viscosity.

In the weaving and spinning of textile fabrics it often happens that some of the lubricating oil used for the machinery drops on to the goods. If it be a pure mineral oil it is very difficult to remove; but if 15-25% of a fatty oil be added to the mineral lubricant, during the subsequent scouring operations its removal from the goods by emulsification is easily effected.

Lubricating Greases.—These are usually made by adding to mineral oils substances known as "oil thickeners." The latter are soaps, made by decomposing some fatty oil with an alkali, caustic soda or lime; or, sometimes, precipitated aluminium soaps are employed and these dissolved in the oil.

Another method of preparation consists in adding some fatty oil or fatty acid (commercial oleine, etc.) to a mineral oil and then saponifying the mixture by the addition of soda or lime-water. Many of the cheaper greases are made from rosin oil and lime or soda, or from rosin, mineral oil and lime or soda.

Tallow, mixed with graphite, soapstone, kaolin or even barytes, is also used in making cheap wagon greases, etc. Sulphur, too, is fraudulently added to render fatty oils more viscous, but this is both dangerous to the bearings (corrosion) and might cause fire.

Very cheap lubricating greases are made from coal tar, dead oils, anthracene oils and creosote oils, but as those have often a very low flashing-point and, when once inflamed, are extinguished with great difficulty, their use must be considered as very dangerous; they are inadmissible as lubricants for indoor purposes.

Reference may also be made to the practice of "deblooming" mineral oil. Almost all mineral oils have a characteristic greenish fluorescence or "bloom." If certain nitro compounds, such as nitro-naphthalene, be dissolved in the oil, this "bloom" is destroyed, and such "debloomed mineral oils" are often used as adulterants for fatty oils, increasing, if of low flash-point, the danger of fire.

Cooling Heated Bearings.—When the oil supply in a bearing runs short, it quickly becomes heated by the friction between the journal and the brasses. If, to such a hot bearing, fresh oil be run in, no marked cooling results, because the heat so lessens the viscosity of the oil that it is squeezed out from between the metallic surfaces. It is to such heating of bearings that many fires have been traced, and it is of interest to consider what methods are adopted for cooling the bearings by machinists.

(a) The most obvious method is to pour water over the heated part and, when cool enough, to give the bearing an ample supply of fresh oil. Where this can be used it is undoubtedly the best method, although if very hot the metal work is not improved by the application of water and, in any case, the water tends to rust the machinery.

(b) Some engineers run a strong soap solution into the bearing. The heat causes the water to evaporate, and the soap left behind is sufficiently viscous and resistant to heat to lift the axle out of contact with the brasses, whereby the friction is reduced and the cause of heating is removed. If the bearing be very hot the evaporation of the water may take place with almost explosive violence, and the soap left behind may undergo destructive distillation, so it is best to cool the bearings by external application of water before running in the soap. When cool the soap should be washed out of the bearing by a plentiful application of the ordinary lubricant, otherwise clogging may occur.

(c) A common method of cooling is to mix some flowers of sulphur with the lubricating oil, and to pour the mixture into the bearing. Under the influence of heat sulphur attacks the oil, producing viscous, rubber-like substances, which form a film between the axle and the brasses, so that the cause of heating, the friction of metal on metal, is removed. Sulphur acts more effectually where fatty oils are employed as lubricants than with mineral oils, so instead of mixing the sulphur with the lubricant (if it be a mineral oil), castor, rape, lard, neatsfoot or sperm oil is often substituted with good results. The use of too much sulphur should be avoided, as it acts injuriously on the brasses, and when the bearings are cool it should always be washed out by the addition of some of the usual lubricant or, better, by some fatty oil.

(d) A mixture of the lubricant or other oil with black lead is also found very effective. The black lead, a solid, is not affected by the heat of the bearing, and so is able to form a film which will sever the metallic contact between the axle and the brasses. The bearing soon cools, when fresh lubricating oil may be run in. Black lead is without action on the metallic surfaces and does not clog.

Crookes, some years ago, patented a scarlet paint, consisting of a double iodide of mercury and copper, $HgCu_2I_4$, which, on heating to 150° F. (65.5° C.), changes to black. This should prove very useful for indicating a rise in temperature in a bearing.

OILS IN THE LEATHER INDUSTRIES.

In currying and softening leather, in the preparation of chamois leather, etc., oils find considerable application. Among those employed may be mentioned—

(a) *Japanese fish oil tallow* or *sardine oil tallow,* obtained by cooling fish oil or allowing it to stand for some time after heating for 1-2 hours at 50-60° C., when it separates into three portions—a liquid upper clear layer, a solid middle layer and a lower one, consisting of albumenous portions of the fish. The middle solid fat is largely used in preparing leather and in currying.

(b) *Menhaden Oil.*—This is prepared in large quantities from the heads and intestines of an American fish by the usual process. (See oils, p. 159.) Its power of absorbing oxygen is so great that it ranks as a drying oil, and consequently is especially liable to develop heat under favourable conditions. Its constants are specific gravity, 0.927-0.933; saponification value, 192; iodine value, 148-160. Maumené's test, 123-128° C. It is used in currying and making sod oil or degras.

(c) *Cod Liver Oil.*—Theoretically prepared from cod livers, but often adulterated with other fish oils, as ling liver, hake liver, haddock liver, etc. Several varieties are met with in commerce.

Brown Oil.—A genuine cod liver oil, but extracted from more or less putrid livers by the usual process. (See oils, p. 159.) There are several brands, as "Newfoundland" and "Norwegian" cod liver oil. By cooling, "fish stearine," largely used in currying, is obtained.

Coast Oil.—This is prepared from the various fish which come to the net of the trawler. According to the temperature used in the manufacture, the oil contains more or less "stearine," which it deposits on cooling. This brand of oil is the chief cod liver oil used in the leather industry.

Other liver oil, as skate and shark liver, are employed in currying, etc.

(d) *Blubber Oils.*—In the dressing of leather the oils extracted from the blubber of seals and whales find extensive application. The latter is often adulterated with the former and also with rosin oil.

The blubber oils are also often known under the general name of "train oil." (Constants, see table, page 158.)

(e) *Bone Fat.*—Obtained by boiling bones with water. This oil is non-drying and does not easily turn rancid.

(f) *Japan wax* is a true glyceride and not a wax. It forms a pale yellow, hard substance, smelling of tallow and beeswax and melting at 50-56° C. (122-133° F.), and is used in polishing leather.

It consists essentially of glycerine palmitate and contains no liquid oleine. Iodine value, 4.2.

Sod Oil or Degras.—In the preparation of chamois and other leathers the skins are, after liming, freeing from hair and "drenching" with fermented bran infusions, smeared and well rubbed with some of the above oils, generally whale or cod oil. After exposure to air more oil is rubbed in until the skins have taken up some 50-60%, some of which appears to combine with the leather. The excess is removed from the skins, either by pressing, wringing and treatment with dilute alkaline solutions (caustic soda or sodium carbonate), or by the two former operations and immersion in hot water.

On adding acid to the scouring solutions after use in the first process "sod oil" is obtained, while the oil obtained from the second method of procedure forms "degras," or "moëllon."

The oil thus prepared contains, in addition to the oxidation products of the oils used, unchanged oil, resinous oxidation products and more or less water (15-40%).

The "artificial degras" or "degras substitutes" of commerce consist of a mixture of fish oils, low-class tallows, rosin oil, various oleines and recovered greases, vaseline, etc. Drying or semi-drying seed oils, too, are sometimes present, but their use, as well as that of rosin oil, is to be objected to, as they are apt to cause overheating of the leather when stored in heaps. Degras is used in currying or dressing of tanned leather.

SPONTANEOUS COMBUSTION OF LEATHER.

In a recent paper* Professor Eitner, writing on this subject, states: "As doubts exist as to the dangers of outbreaks of fire through spontaneous combustion, people take no precautions against its occurrence. The beginning of many fires in tanneries is in the currying shops and particularly in the stuffing room, on account of the quantity of grease and fat present. At the end of last winter I had, at the Vienna Leather Industries Laboratory, an opportunity of observing how a fire can originate in the stuffing room. Some woollen cloths which were saturated with cod oil were placed in close proximity to a steam-pipe. Suddenly an intense odour was given off from the cloths, which had turned brown. Owing to the heat generated and to the rapid oxidation of the oil they burst into flame. In the stuffing room, on goods impregnated with cod oil coming into contact with any hot substance, the oxidation of the oils is forced, and flames are the result. Finished leather, impregnated with cod oils, can certainly from the same cause be ignited. Danger can also arise from the oil wipers used for cleaning the stuffing tables. Other fats, such as tallow, mineral oil, moëllon, rosin oils, used for stuffing, are comparatively not dangerous."

Menhaden oil and some of the whale and seal oils, as well as seed oils, are, in the authors' opinion, also very liable to give rise to fire in a similar manner.

It would be very instructive to examine many of these oils when spread on ground leather or leather cuttings in the apparatus employed by Mr. Mackey for cloth oils. (See page 185.) In some leather processes, however, the use of oxidisable oils is essential.

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* See abstract, *Jl. Soc. Chem. Indus.*, 1898, p. 1201.

The iodine value also proves a useful criterion for examining oils here, as well as in the case of cloth oils.

OILS IN THE TEXTILE INDUSTRIES.

WOOL.—It is usual to add to the wool some 10-15% of oil to facilitate the spinning operations. In the shoddy industry, too, rags are invariably oiled before being subjected to grinding or pulling. In Belgium castor-oil soap or neutralised turkey red oil (see dyeing) has largely and advantageously replaced the oils proper, and on the continent, generally, neutral oils and oleic acids emulsified by sodium carbonate or ammonia are used for these purposes.

The oils employed for greasing wool are—first and best, olive oil (Gallipoli); then lard oil, oleine (commercial oleic acid prepared from many waste greases by saponification or distillation), black recovered oil, seek oil and brown grease oil (from the "cracked" alkaline scouring liquors in woollen mills).

A good cloth oil should be easily removed by scouring, consequently linseed and rosin oil or other drying oils which oxidise on the fibre should on that account be avoided.

Hydrocarbon or mineral oils are not of themselves soluble or emulsifiable in alkaline scouring solutions, hence they cannot be used alone, but if 15-25% or more of a fatty oil be mixed therewith they are easily emulsified and thus removed.

Far more important to us is the development of heat which oils show when finely distributed over wool or other fibrous material. The large surface offered by the oil greatly increases the rapidity of absorption of oxygen from the air, *i.e.*, the oxidation of the oil with corresponding production of heat. If adequate cooling be not provided, *e.g.*, where bales or heaps of greased wool are stored, the temperature may rise to the ignition point of the oil or material and so spontaneous inflammation of the mass may arise. Unless stored closely in bulk there is little danger, as the heat produced is rapidly carried away by the air.

In their oxygen absorption, as already stated, the oils differ greatly, and consequently the heat produced by their exposure to air when spread on wool or other porous mass also varies, so that some oils are very prone to cause fire, while in others this tendency is absent.

Further, there must be taken into account that during many of the operations the oiled yarn or fabric may be exposed to such temperatures that if an oil of low flash-point were employed, additional risks of fire would arise.

Taking the above facts into consideration, before it can be decided whether an oil may be used with safety the following properties must be carefully studied:

(1) *The Flash-Point.*—An oil should not flash below 167.8° C. (340° F.). None of the pure fatty oils flashes below this temperature, but, as already intimated, many of the mineral oils do, although if carefully prepared, mineral oils of higher flash-point can be easily obtained.

(2) *The Quantity of Unsaponifiable Matter.*—Insurance companies are accustomed to assess the premium paid for fire risks on works partly by the quality of the oils used. Their measure of "quality" is the quantity of unsaponifiable matter (generally, but not always, be it remembered, consisting of mineral oil). Thus in woollen mills—

No extra charge is made where olive (Gallipoli) oil, lard oil, oleine ("saponified" or distilled) not containing more than 10% unsaponifiable matter, fish oil or a manufactured oil containing not more than 30% unsaponifiable matter and flashing above 167.8° C. (340° F.).

A higher rate (50% extra) is charged for oil containing above 30% unsaponifiable, but below 50%.

A still higher rate (75% extra) is made for black recovered oil below 50% unsaponifiable.

The highest rate (200% extra) is charged for oils containing above 50% unsaponifiable matter or mineral oil, pine or rosin oil, linseed oil, rape, cotton or other seed oil or any mixture thereof.

The reasons for objecting to the presence of unsaponifiable matter, *i.e.*, mineral oil, are not very obvious, but appear to depend partly on its low flash-point, but more on its small viscosity or greater fluidity whereby it tends to spread itself over a building to a greater extent than a fatty oil would do, so that if a fire is once started in a mill where it is used greater difficulty is experienced in extinguishing it.

Except for the above reasons, the authors fail to see on what the objections are founded, for mineral oils, as will be shown, are less susceptible to spontaneous combustion than are the fatty oils.

Liability to Cause Spontaneous Combustion.

Obviously the drying or even semi-drying oils are inadmissible as cloth or textile oils, for they show great tendency to oxidise in air, producing a corresponding amount of heat.

Some valuable information may be obtained by determining the oxygen absorption (Livache method) or the iodine value, but more useful is a direct method of determining the dangers of firing or heating of oils which has been devised by Ordway.* At the instigation of some

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* Richards, *Jl. Soc. Chem. Indus.*, 1892, p. 547.

cotton manufacturers and fire insurance companies in America Mr. Richards undertook his investigation.

The apparatus employed consists of a 6-inch iron tube closed at both ends with wooden discs, into which a narrower (4-inch) tube is inserted, with metal covers at each end to support it. There is thus an air space of 1 inch left round the tube and 3 inches at each end. The whole apparatus may be heated by a Bunsen burner. Three thermometers are inserted into the inner shell, which allow the temperature to be read off.

To test an oil or mixture of oils, 50 grammes of it are evenly distributed over an equal quantity of cotton waste or other material. The oiled waste is then placed in one end of the inner tube, the thermometer inserted into the interior of the ball and a second plug of unoiled waste placed at the other end. On heating the middle of the tube the thermometer in the unoiled waste is allowed to rise to 100-101° C., and then the temperature of the other thermometer is read off.

It is stated that the results obtained with this apparatus are of the greatest value in determining the cause of or risk of fire with different oils, or the percentage of a fatty oil which may safely be added to a mineral oil.

More recently W. McD. Mackey has communicated a series of papers to the Society of Chemical Industry* on the spontaneous combustion of oils spread on cotton, in which he describes an apparatus which may be used for examining oils for their liability to cause fire.

The apparatus, Fig. 40, consists essentially of a cylindrical double-jacketed copper water bath closed by a tightly fitting lid, which latter contains three perforations, one in the centre for a thermometer and two near the opposite edges, through which two tubes pass, one descend-

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* *Jl. Soc. Chem. Indus.*, 1894, p. 1164; 1895, p. 940; 1896, p. 90.

ing nearly to the bottom of the chamber and the other an ascending tube, whereby a slow current of air through the apparatus is maintained.

Into a cage of wire gauze, 7 grammes of cotton wool, soaked in 14 grammes of the oil to be tested, are introduced and the thermometer inserted into the centre of the mass. The water in the bath is brought to boiling and the cage thus charged is placed in the inner chamber. After one hour's heating the temperature indicated by the thermometer is taken.

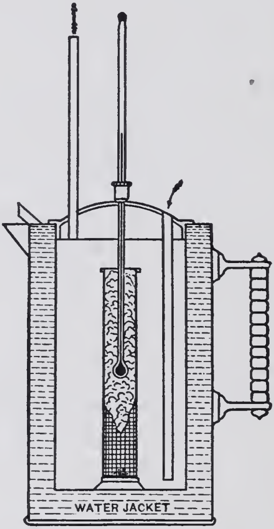

FIG. 40.—Mackey's Oil Tester.

From experiments with this and other forms of the apparatus Mr. Mackey concludes that the free fatty acids exert more charring on cotton (hence are more liable to spontaneous combustion) than the oils themselves.

Some of his results with various oils are given in the following table, the temperatures being expressed in centigrade degrees.

Oils used.	Temp. in 1 hr.	Temp. in 1 hr. 15m.	Temp. in 1 hr. 30m.	Max. temp.
Cotton seed	121°	242°	282°	284° in 1.35
Olive, fatty acids	102°	135°	208°	226° " 1.45
White Australian oleine	103°	115°	191°	230° " 1.45
Olive	98°	102°	104°	241° " 3.25
Oleine	98°	101°	102°	110° " 2.8
97% Oleine	98°	100°	102°	172° " 3.15
Neutral olive	98°	100°	101°	235° " 5.16

It is considered that any oil showing a temperature of above 100° C. in 1 hour is dangerous, consequently the first three would be so classed, while the remaining four are "safe" oils.

Mr. Mackey further finds that the addition of mineral oils to a fatty oil reduces the liability to spontaneous combustion. The free acids of an olive oil used alone gave a temperature of 113° C. in 1 hour, 194° C. in 1 hour 30 minutes and a maximum temperature of 208° C., but when mixed with 25% American mineral oil the temperatures indicated were 95°, 98° and in 5 hours and 45 minutes 111.5°. He is consequently of the opinion that the insurance companies lay too much stress in their regulations on the dangers arising from use of mineral oils in textile factories.

A few words regarding the special oils used in the cloth trade may not be out of place.

Oleine or commercial oleic acid is obtained as a by-product in the preparation of stearic acid in the candle industry. The tallows and other fats are saponified by alkalies or steam and the free fatty acids obtained. They are then chilled when the solid acids, stearic and palmitic, crystallise out and are removed from the liquid oleic acid by filtration. When thus prepared the "oleine" forms a yellow or light brown liquid, and often contains, in addition to oleic acid, notable quantities of stearic and palmitic acid, which cause it to become partly solid in cold weather. An oleine prepared from cottonseed "stearine" would contain, in addition to oleic acid, large quantities of the other acids present in cottonseed oil, namely, linolic, etc., which are drying acids.

Impure and discoloured oleines containing more or less unsaponifiable matter are prepared from many waste fats, as wool fat, cottonseed "foots," "cracked" soap and scouring liquors, etc., either by cooling and filtering in bags under pressure or by distillation.

WOOL FAT is obtained by "cracking" the wool-scouring suds with acid (vitriol), removing the fatty matter from the surface and filtering it. It contains the free acids of the wool fat, some undecomposed fat and certain alcohols (cholesterol, etc.). From it "lanoline," used for the toilet, and cruder products, used for leather stuffing, are obtained.

YORKSHIRE OR BROWN GREASE is similarly produced by souring or cracking with acid the various suds obtained in the scouring of wool and woven goods. It consequently contains not only the acids, etc., of wool fat, but also the fatty acids of the soaps and oils used in scouring, spinning or other operations through which the wool has passed.

DISTILLED GREASE.—When wool fat or Yorkshire grease is distilled in a current of superheated steam there passes over an "oleine," used as a cloth oil, and a "stearine," used for stuffing leather and for soap. The oleine contains, in addition to various free acids, a quantity of hydrocarbons produced by their destructive distillation and also cholesterol. These hydrocarbons have been but little studied, but they are probably almost identical with those contained in petroleum and shale oil.

Seek oil is a grease recovered by souring the mixed suds of the scourings of wool, silk or cotton (turkey red dyeing), and must of necessity vary in composition with the soaps and oils used in the works from which it is obtained. According to its purity, it is used in soap making or distilled to yield a "cloth oleine."

Black recovered oil is similarly obtained from the greasy waste of woollen mills. Its composition is very variable, containing as it does the fatty acids of wool fat, the soaps and oils used in the various processes and also often some of the machinery lubricating oils.

As many of the soaps used during the different operations in mills are made from any fatty substance, including "cottonseed foots," "linseed oil foots" and other oily refuse, the fatty acids obtained therefrom are contaminated with many of the drying fatty acids, and consequently the oleines, etc., prepared by souring and filtering, etc., will contain these acids. On account of their oxygen absorptive power such oleines may be dangerous. Those obtained from the greases by distillation are thought by some to be less so.

In view of these considerations, it is desirable that the manufacturer should either use soaps, such as castor-oil soap, which are not made from drying oils, or keep the soap liquors separate and "crack" them independently.

In mills where the manufacture of union goods, *i.e.*, fabrics made from mixed cotton and wool, and rag grinding of union rags in mungo and shoddy mills, is carried on, oils which have little or no action on cotton should be employed. Or before grinding mixed cotton and wool rags the cotton should be removed by "carbonising" (extract wool). As already stated, not only is cotton of itself more easily inflammable, but it is also more affected by the free acids of oils than wool, and consequently more liable to spontaneous combustion. The use of free oleic acid (commercial oleines) is therefore objectionable, and where cotton is handled, only pure neutral oils, such as olive, lard, etc., or mixtures of these with mineral oil or such "safe mixtures" of oleine and mineral oil as have been mentioned, should be employed as cloth oils.

EMULSIFIED OILS.—Alkaline solutions, such as sodium carbonate or ammonia, have the power of holding oils in suspension in a very fine state of division. This they do, probably, by partially saponifying the oil. Such oil emulsions will also emulsify mineral oils; oils which are slightly rancid, *i.e.*, contain free acid, are also better capable of emulsification than the neutral oils and will hold more mineral oil in suspension.

These facts are taken advantage of in the manufacture of cloth oils, especially on the continent. Rancid olive oil or lard oil with a little commercial oleine or turkey red oil, etc., is agitated with sodium carbonate or ammonia solutions and with more or less mineral oil. The emulsions thus obtained are used for oiling wool, etc., and have the advantage of being easily removed during scouring and washing.

Their use is attended with but little risk of fire, provided that no excess of a drying oil has been used in their manufacture.

OILS IN DYEING.

The use of fatty matters by the dyer to fix or brighten his colours is of very ancient origin. The Hindoos employed milk for this purpose, and now the turkey red dyer (which colour is the modern representative of the madder red of the Hindoos) makes use of certain oils for a similar purpose. Further, many basic dyestuffs obtained from coal-tar are dyed on an oil mordant.

Olive oil, chemically, essentially trioleine $C_3H_5(C_{18}H_{33}O_2)_3$, is a clear, faintly yellow or greenish liquid. (For constants see table p. 158.) When exposed to air for any considerable period it becomes rancid by the absorption of oxygen and liberation of the fatty acids. On boiling with caustic alkali solution it is completely saponified, but when merely shaken therewith or with an alkaline carbonate, as soda, only partial decomposition takes place, and the whole of the oil and solution is converted into a milky liquid or emulsion, in which the former is held suspended in an extremely finely divided state. A rancid olive oil, *i.e.*, one containing free fatty acid, shows this property to a markedly greater extent, and such an oil is sometimes called emulsive oil. By treatment with concentrated sulphuric acid at temperatures below 40° C. olive oil is converted into a very complex substance containing hydroxy-oleic acid, hydroxy-oleic-glycerine-sulphuric acid, etc., readily soluble in dilute alkalies. (See Turkey red oils.)

Olive oil finds application in dyeing Turkey red by madder or alizarine on cotton yarn or cloth and is also employed as a mordant, etc., for certain basic aniline colours. There are two chief methods in use, viz.—

The Emulsion Process.—This is chiefly employed for dyeing yarns. Without entering into details, it consists essentially in repeatedly treating the cotton with emulsions of olive oil and sheep's dung (used on account of its alkaline character), when it takes up some 30% of oil, excess of which is removed by steeping in dilute sodium carbonate solution and wringing, exposing the oiled material to the air or drying it in stoves, mordanting and finally dyeing.

Steiner's Process is used for dyeing calico or cotton cloth. The goods in open width are padded with olive oil heated to 110° C. (230° F.) and then stoved for two hours at 70° C. (158° F.), whereby the oil is oxidised on the fibre. Excess of oil, *i.e.*, the unoxidised portions, is then removed by a gentle scouring with dilute sodium carbonate solution and the goods mordanted and dyed as usual.

The dangers of fire in these two processes depend on the heat evolved during the oxidation of the oil on the fibre. This heat only becomes dangerous when it is prevented from dissipating as quickly as it is liberated, either by the defective ventilation of the stoves or by allowing the goods to lie, closely packed, as heaps of yarn or rolls of calico, when they have been freshly oiled or immediately after removal from the stove, before the oxidation is complete. (See also aniline black dyeing.)

Another source of danger consists in the overheating of the stoves, for then the oxidation proceeds too rapidly and heat sufficient to raise the cotton and oil to their ignition point may be produced. The authors have been informed that sometimes a stove ignites if the doors are suddenly opened so as to admit the air. Such an event could only take place in an improperly ventilated stove, where it is possible, though hardly probable, that the inrush of air might bring about such rapid oxidation as to cause ignition.

In practice the person in charge of a stove can tell by the peculiar acrid smell produced if its temperature is too high, in which case he opens the ventilators to cool it by an ample supply of fresh air. A properly constructed stove should be provided with effective means of ventilation.

The cheaper varieties of olive oil of commerce are frequently adulterated with cottonseed and other semi-drying or drying oils, whereby they are rendered more dangerous, besides being inferior for dyeing purposes.

The emulsive oils, such as are used in the old emulsion process, appear to be less suitable for use in the Steiner process, for the free fatty acid which they contain, renders them more liable to generate heat and char the fibre during stoving. (See cloth oils.)

TURKEY RED OILS.—The complex mixture of substances produced by the action of concentrated sulphuric acid on olive and castor oils finds extensive use in the dyeing of madder, alizarine or Turkey red, and hence is known under the general name of *Turkey red oils.* The nature of the changes taking place during this reaction is much too complicated and theoretical to find more than mention here, but it may be noted that they are of the following kinds:

(a) Oxidation of the unsaturated fatty acids.

(b) Liberation of these acids, union of the sulphuric acid with the glycerine set free and also partial combination of the hydroxy fatty acids with sulphuric acid, or, in other words, the production of free acids containing combined sulphuric acid.

By washing the product of the interaction with water and adding strong brine, the free fatty acids, unchanged oils and the sulphated acids rise to the surface and are removed from the other products. They are then partially neutralised with soda or ammonia, and form, in this state, an emulsion which may, if properly prepared, be added to water without producing a precipitate. Separation of solid matter shows the presence of cottonseed oil or rape oil.

By treatment with alkali and brine or with hydrochloric acid and brine or hot water, the compound sulphuric acid is split up, alkaline salts of the acids in the first case, or in the two latter cases the free acids themselves and glycerine being produced.

The commercial Turkey red oil consists of such a partially neutralised mixture as has previously been mentioned, and is known, in addition to the name already used, as alizarine red oil, sulphated oil, soluble oil,* etc.

APPLICATION OF TURKEY RED OILS TO DYEING.—Oils have found but little application in mordanting or dyeing the animal fibres; but both woollen and silk goods are sometimes treated, *after* dyeing, with Turkey red oil, an emulsion of olive oil or soap solution to soften them and correct their harsh feel. This is especially the case with weighted silk, where soaping is frequently resorted to.

In calico or cotton cloth dyeing the fabric is simply padded with a neutralised solution of Turkey red oil, dried and then steamed under pressure. After dyeing the goods are usually impregnated with the neutralised oil, steamed, soaped, etc., for clearing.

In calico printing sulphated oil also finds extensive use in preparing cloth for steam alizarine and steam aniline colours containing tannic acid, where it acts partly as a brightener and partly as a fixing agent.

A few words about the changes which may take place during the steaming and stoving. Under the influence of the steam in the chamber, some of the ammonia which has been used to neutralise the Turkey red oil is volatilised, and the free fatty acid, glycerine and ammonium sulphate are liberated on the fibre. If, on the other hand, soda or potash solution of the oil be employed, only a portion of the fatty acid and glycerine is liberated, while the sulphuric acid and the remainder of the fatty acid are converted into their sodium or potassium salts.

The liberation of the oxidised fatty acids is desirable, because thereby better penetration of the oil into the

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* **Under "soluble oil," in commerce, castor-oil soap is often understood.**

fibre and, by its being oxidised therein, a better fixation is obtained. For this reason the ammonia neutralised oil, as more easily decomposable, is preferred by most dyers; the sulphuric acid set free combining with some of the ammonia to form sulphate (which is not so easily split up by the heat as the ammonia salts of the fatty acids), is prevented from exerting any charring action. If an imperfectly neutralised oil be employed, *i.e.,* an emulsion of Turkey red oil with saponified or neutralised oil, there is not sufficient ammonia or soda to combine with the liberated sulphuric acid, and injury to the fibre will probably result. It would appear, however, that there can be but little danger of fire taking place during steaming, since the air is almost wholly excluded; but, if after steaming, the goods are imperfectly washed, so that the sulphuric acid is not completely removed, during the subsequent stoving processes tendering of the fibre or even charring may result. Still, actual fire in the process is hardly possible from this cause. The presence of cotton-seed or other semi-drying oils, or, rather, their fatty acids as adulterations of the Turkey red oil, increases the risk of fire and also the danger of spontaneous inflammation of the oiled cotton when lying in heaps (yarns) or rolls (calico) in the warm atmosphere which usually obtains in the dye-house.

The employment of sulphated oil in dyeing Turkey red on cotton is attended with much less risk than the old emulsion or Steiner's processes.

CHAPTER XI.

VOLATILE SOLVENTS AND COAL-TAR PRODUCTS.

Ether—Alcohol—Methylated Spirit—Wood Spirit—Acetone—Chloroform—Carbon Tetrachloride—Fusel Oil—Carbon Disulphide—Turpentine—Rosin Spirit—Rosin Oil—Tar Distillation—Coal Tar—Dehydration — Rectification — Products — Benzene — Toluene-Xylene — Solvent Naphtha — Distinction between Benzene and Benzine—Naphthalene—Anthracene—Carbolic Acid—Creosote—" Dead Oil."

A GREAT variety of volatile solvents find application in the arts, but as a description of their methods of production would occupy too much space, only their most important properties and uses will be indicated here. They are all organic compounds, that is, contain carbon, and are, with few exceptions, inflammable.

ETHER $(C_2H_5)_2O$, sometimes called sulphuric ether, forms a very volatile, colourless, sweet-smelling liquid, boiling at 34-35° C. (93-95° F.). It has a specific gravity, when pure, of 0.736 at 0° C. (32° F.), is slightly soluble in water (10 per cent.) and will mix with alcohol in all proportions. Perhaps its most remarkable property is its great volatility, even at temperatures much below its boiling point. Its vapours are very inflammable, and are heavier than air, consequently no flame should be brought in the neighbourhood of any vessel containing it. The authors have seen cases of ether fires where the igniting flame has been situated many feet from the vessel of ether.

It is used as a solvent for many resins (in photographic varnishes, etc.) and for nitro-celluloses used in the manufacture of celluloid, collodion, artificial silk and some explosives.

ALCOHOL, ETHYL ALCOHOL (C_2H_5OH).—A colourless liquid of characteristic odour and taste, boils at 78° C. (172.4° F.) and has a specific gravity of 0.793. It is inflammable, but not so much so as ether. Pure alcohol, owing to the duty, is very expensive, and only finds limited use. "Rectified spirits of wine," the commonest commercial form, contains 86% of real alcohol. The continental "potato spirit," which is produced in immense quantities by the fermentation of potato starch by malt and yeast, contains 96% real alcohol.

If rendered unfit for human consumption by the addition of 10% wood spirit and ½% petroleum, the excise authorities permit, under certain regulations, alcohol to be sold duty free. It is then known as "methylated spirit," and is largely used as a solvent.

METHYLATED SPIRIT dissolves many gums and resins, forming spirit varnishes, and is also employed in the preparation and application of many coal-tar dyes and as a fuel in spirit lamps or stoves.

Pure alcohol is miscible with water, ether, chloroform, benzene and carbon disulphide in all proportions, but not with petroleum and shale products. Methylated spirit when added to water gives a cloudy solution, because the petroleum used in "denaturing" it, is insoluble in that medium. When poured into coal-tar benzene or carbon disulphide a cloudy solution is likewise obtained, since these two substances will not dissolve the water which the methylated spirit contains.

Both alcohol and methylated spirit or any liquid containing either of them (as brandy, whiskey, etc.) are, in this country, sold as so many degrees "over or under proof." Thus, to take an example, say an alcohol is quoted as 60° over proof. This means that if 100 volumes of the spirit were mixed with 60 volumes of water "proof spirit" would result. Proof spirit is a survival of the times when no accurate methods of testing the quantity of alcohol contained in a liquid were known, and is such a spirit that, when poured over gunpowder and set alight, will just not inflame the powder! It contains 49.24% alcohol, and has a specific gravity of 0.9198 at 60° F. Methylated spirit, as usually sold, is 64° over proof, has a specific gravity of 0.821 and contains 90% of alcohol.

WOOD SPIRIT (crude methyl alcohol, CH_3OH).—In the dry distillation of wood, besides acetic acid and tar, a volatile liquid is obtained; it is separated from the tar, neutralised with slaked lime and the crude wood spirit distilled off, leaving a residue of acetate of lime. By a second treatment with caustic lime, followed by sulphuric acid and redistillation over lime, further purification is effected. Thus prepared, the wood spirit contains from 50 to 95% of methyl alcohol and also acetone, forming a limpid liquid, tinged with yellow, due to the presence of impurities (pure methyl alcohol being colourless). It boils between 55° and 60° C. (131-140° F.), has an unpleasant taste and peculiar empyreumatic odour. Like ordinary alcohol, it is inflammable, having even greater volatility, flashing at ordinary temperature. Largely employed as a solvent in the manufacture of lacquers, varnishes and polishes.

ACETONE (CH_3COCH_3).—Present in wood spirit, but is generally obtained by the dry distillation of acetate of lime. It is a colourless, mobile liquid, having a pleasant, sweetish odour and burning taste, boiling at 56° C. (132.8° F.) and is very inflammable. Acetone is employed partly as a raw material for making chloroform and iodoform and partly as a solvent in the manufacture of explosives.

CHLOROFORM ($CHCl_3$).—A limpid liquid with a sweetish smell, boiling at 61° C. (141.8° F.). Under ordinary conditions it is not inflammable. Its price is prohibitive of its employment in the manufacture of any but expensive varnishes, although it is a most excellent solvent for all fats and resins. Its medicinal uses do not fall within the scope of this work.

CARBON TETRACHLORIDE (CCl_4).—A pleasant smelling liquid, boiling at 76° C. (168.4° F.) and having a specific gravity of 1.63. Carbon tetrachloride forms a most excellent solvent for resins, fats and many kindred substances, and has the great advantage over almost all other volatile solvents of being non-inflammable. In the event of the discovery of a cheaper method of production, this substance would probably be used to the exclusion of many others.

FUSEL OIL.—This substance is obtained as the "last runnings" in the distillations of spirituous liquids. It consists of a mixture of alcohols, amyl alcohol ($C_5H_{11}OH$) being the chief constituent, and forms an oily liquid generally slightly yellow in colour, of an odour reminding one of fruit but at the same time unpleasant, its vapour producing coughing. It boils between 120-140° C. (248-364° F.) and is very inflammable. Used in the manufacture of lacquers, etc.

CARBON DISULPHIDE (CS_2).—The product of the action of sulphur vapour on glowing charcoal or coke. The commercial article forms an evil-smelling, very mobile and highly refractive liquid. When pure, carbon disulphide is colourless and has a peculiar but not unpleasant ethereal odour; it boils at 46° C. (82.8° F.), and has a specific gravity of 1.262. It will mix in all proportions with ether and benzene, but only with absolute alcohol, not with methylated or aqueous spirit.

Carbon disulphide is extremely inflammable, burning with a blue flame to form carbon dioxide and sulphur dioxide in air. Most remarkable is the very low ignition temperature of this substance, a temperature much below that of red heat being sufficient to cause inflammation of the mixture of its vapour with air. (See page 13.)

As an endothermic compound, too, carbon disulphide can, under certain conditions, be exploded by shock (detonation or percussion), and as its flash-point is very low, it forms one of the most dangerous substances used in the arts.

Carbon disulphide is an excellent solvent for all fats and resins. It is used in the cold vulcanisation of rubber, in extracting oils from seeds and waste oily material, in "dry scouring" of wool, etc.

Messrs. Cross, Bevan and Beadle* have discovered a remarkable action of carbon disulphide upon "Mercerised" cotton (*i.e.,* cotton or other form of cellulose which has been treated with caustic soda solution). If this substance be treated with the vapour of carbon disulphide at a temperature of about 80° C. (176° F.) a yellow, plastic mass (cellulose thiocarbonate or xanthate) is obtained, which will dissolve in water, giving a solution of enormous viscosity and capable of depositing the cellulose by a process of coagulation. The solution can be used as a substitute for glue or paste, or as a size for paper or calico. The coagulated substance can be given a variety of forms, and has been employed for book coverings, fancy boxes, artificial leather, upholstery, embossed hangings, etc.; or if mixed with other materials, *e.g.,* ground wood, various

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* *Jl. Soc. Chem. Indus.,* 1893, p. 498; 1894, p. 900.

fibres or clay, it may be used for floor coverings, insulating material, etc.

The danger in this manufacture lies in the use of the highly inflammable carbon disulphide, the finished product being no more inflammable than ordinary cotton. For the manufactured article the name "Viscose" has been suggested.

SPIRITS OF TURPENTINE ($C_{10}H_{16}$), called, also, "oil of turpentine" or simply "turpentine," is obtained by distillation of the crude substance (which exudes from various coniferous trees) with steam. A mixture of the oil and water collects in the receiver and rosin or colophony remains as a residue in the still.

There are three chief varieties of turpentine oil met with in commerce—American, Russian and French, all of which are obtained from the exudations of pine or coniferous trees by the process above mentioned. Turpentine is a mixture of hydrocarbons of the formula $C_{10}H_{16}$. These hydrocarbons on analysis show the same percentage composition, but possess different properties, as boiling point, specific gravity, action on polarised light, behaviour toward chemical reagents, etc., and are known in chemical phraseology as *isomeric modifications,* their different behaviour being explained by attributing to them different molecular structure.

French and American turpentine are very similar in some of their properties; they boil at 155-160° C. (311-320° F.) and have a specific gravity of 0.864-0.870. They differ in their action on polarised light and in the rapidity with which they absorb oxygen from the air, the American variety having the greater absorptive power. French turpentine contains the isomer known as *laevo-pinene,* because it turns the plane of polarised light to the left. American turpentine contains, in addition to this substance, a larger quantity of *dextro-pinene* (rotating the plane of polarised light to the right).

Russian turpentine is of more variable composition than the above. Its specific gravity is from 0.862-0.873, and its boiling point ranges from 156-180° C. (312-356° F.), the greater portion distilling between 171-175° C. (340-347° F.). It has greater power of absorbing oxygen than either of the two former, a stronger odour, and it rotates the plane of polarised light to the right. Essentially, Russian turpentine consists of the isomer *sylvestrene.*

For our purpose, except in those points already mentioned, turpentine may be considered as one substance. It forms a mobile liquid, generally colourless, and has a very characteristic odour; it is insoluble in water, but will mix with almost all other volatile solvents, and has great solvent power for fats and resins.

Turpentine is very inflammable, flashing at 36-38° C. (97-102° F.), burning with a luminous, smoky flame. When mixed with concentrated sulphuric acid a great amount of heat is developed; the turpentine is coloured red brown by the resinous products formed, but the bulk is converted into two substances—terebine (B. P. 160° C. [321.8° F.] formula $C_{10}H_{16}$) which finds use in varnish making as a drier, and colophene $C_{20}H_{32}$, B. P. 300° C. (573.8° F.). Concentrated nitric acid, when added to turpentine, causes inflammation.

A piece of paper or rag soaked in turpentine, if placed in contact with chlorine or bromine at once inflames. Iodine also acts very energetically on this substance.

Turpentine, too, is very susceptible to oxidising agents. When exposed to air it absorbs oxygen, becoming gradually converted into a more or less viscous liquid. When spread in thin layers it evaporates and leaves a resinous oxidation product behind.

Ozone is absorbed by turpentine and the solution has been employed as a disinfectant.

The avidity which turpentine shows for oxygen, and the production of heat during the absorption of that substance, have given rise to cases of spontaneous combustion. Cotton waste soaked in turpentine when left in bulk exposed to air very quickly inflames. A case of fire from such a cause has come to the authors' knowledge. A roll of calico which had been treated with turpentine was accidentally left for some six hours. On unrolling, the interior portions of the roll were found to be charred.

Turpentine is largely used in the arts as a solvent for resins and fats in varnish making, in painting, and also Russian turpentine or, rather, its oxidation products are employed in the manufacture of the disinfectant "Sanitas."

Turpentine is often adulterated, especially that used by house painters, the chief adulterants being rosin spirit, petroleum or shale naphtha and coal-tar naphtha.

ROSIN SPIRIT OR PINOLINE.—Obtained, along with acetic acid and other volatile substances, as the first runnings in the destructive distillation of rosin or colophony. It is a colourless or slightly yellow (old) liquid of very characteristic "piney" odour. Its specific gravity varies between 0.86 and 0.90 and its boiling temperature between 120° C. (248° F.) and 240° C. (464° F.), although many of the cheaper commercial samples contain higher boiling products.

Rosin spirit consists of a very complex mixture of hydrocarbons, some of which belong to the coal-tar naphtha group and some to the turpentines, which latter substances it closely resembles in many of its properties.

It is very volatile and inflammable (flash-point 97-102° F., about the same as turpentine). It absorbs oxygen from the air and resinises, like turpentine, with the production of heat.

The chief uses are as an adulterant and substitute for turpentine in the manufacture of paints and varnishes. Many of the turpentine substitutes now sold under fancy names, such as "turpentyne," "turpenteen," "patent turpentine," etc., are mixtures of this substance with petroleum or shale naphtha or other products.

ROSIN OIL.—Although not a volatile solvent this substance may be well treated here. When the destructive distillation of rosin is pushed further, a thick, reddish, oily liquid of blue to green fluorescence ("bloom") passes over into receivers. This is refined by treatment with sulphuric acid and caustic soda and redistillation, when it is separated into several trade varieties, known as "soft," "hard," etc., rosin oil. These differ in their viscosity, drying power and specific gravity. Iodine value, 55-70; specific gravity, 0.980-0.995; flash-point (c), 266° F.; unsaponifiable matter (*c*), 80%.

Rosin oil finds application in the manufacture of wheel greases, when it is partially saponified by lime or soda, and as a drying oil. Its slight drying power may be increased by suitable treatment, when it forms a brittle, easily fusible coating, which has also the disadvantage of becoming "tacky" on ageing. It is used in making cheap paints and in the adulteration of boiled linseed oil.

SHALE NAPHTHA OR SPIRIT.—As mentioned under petroleum, a volatile spirit is obtained during the distillation of carbonaceous shale as carried out in Scotland and elsewhere. It consists of a mixture of many hydrocarbons, and has a specific gravity of 0.70-0.74, but is generally about 0.73. The commercial article boils between 76-190°

C. (170-374° F.). Flash-point at the ordinary temperature. Shale naphtha is largely used as a solvent for gums and resins in the manufacture of cheap varnishes and as a substitute for turpentine in paint making.

BENZOLINE, BENZINE OR PETROLEUM SPIRIT has already been mentioned under petroleum. The greatest care must be exercised in using shale naphtha or benzoline, as they are both extremely inflammable.

TAR SPIRIT. } (See COAL-TAR DISTILLATION.)
BENZENE. }

COAL-TAR DISTILLATION.

Coal-tar forms the source of many important commercial products and from it are obtained the materials used in a great variety of industries.

The discovery of the formation of aniline from nitrobenzene by Zinin in 1842 and the preparation of mauveine therefrom in 1856 by W. H. Perkin led to the founding of the important coal-tar colour industry, and since that time a vast multitude of useful products has been obtained from the benzene, phenol, etc., contained in coal-tar. A very important industry, namely, the distillation and purification of the crude tar of the gas-works, thus had its origin.

Much misconception has arisen from the term "coal-tar colours," which by the general public is understood to mean that these substances exist as such in the tar. This, of course, is not the case, coal-tar serving only as the raw material from which they are prepared, often by processes of great complexity.

During the distillation of the crude tar, which collects in the hydraulic main of the gas-making plant, many substances are formed which were not present in the tar itself. The products depend largely, not only on the nature of the tar, but also on the temperature and conditions of distillation. The stills are often unequally heated, and the vapours arising from the tar coming in contact with the walls at different temperatures are decomposed, producing very different products.

The operations involved in the purification and rectification are as follows:

(1) *Dehydration.*—After settling or running off the tar from the ammoniacal liquor the former always contains some moisture; it is heated to about 80° C. in large iron cylinders with taps at different levels; by virtue of the difference in density (sp. gr. of crude tar 1.1-1.2) a separation of the greater portion of the water is by this means effected.

(2) *Distillation.*—The dehydrated tar is transferred to the stills, which are of various constructions. Here a separation of its constituents, by what is known as "fractional distillation," takes place. Fractional distillation depends on the properties which mixed liquids show on heating; the one which has the lowest boiling point passes into the distillate first, the others following in the order of their boiling points. In this property the constituents of coal-tar vary greatly. Benzene, C_6H_6, the lowest member, boils at 80° C. (176° F.), and anthracene, $C_{14}H_{10}$, at 360° C. (680° F.). Thus a separation of the ingredients by dividing the distillate into "fractions," depending on the temperature at which they come over, may be effected.

In the accompanying diagram (Fig. 41), the arrangement of the still, condenser and receiver is shown. Many of the substances pass off as gases, so the condenser is usually separated from the still by a wall in order to avoid the ignition of these products by the still-fire, and from the end of the condenser a pipe is sometimes led through the roof of the shed to take them away. The retort is filled nearly full of tar (10-50 tons) and as soon as the distillation starts, especially if the tar is at all damp, the

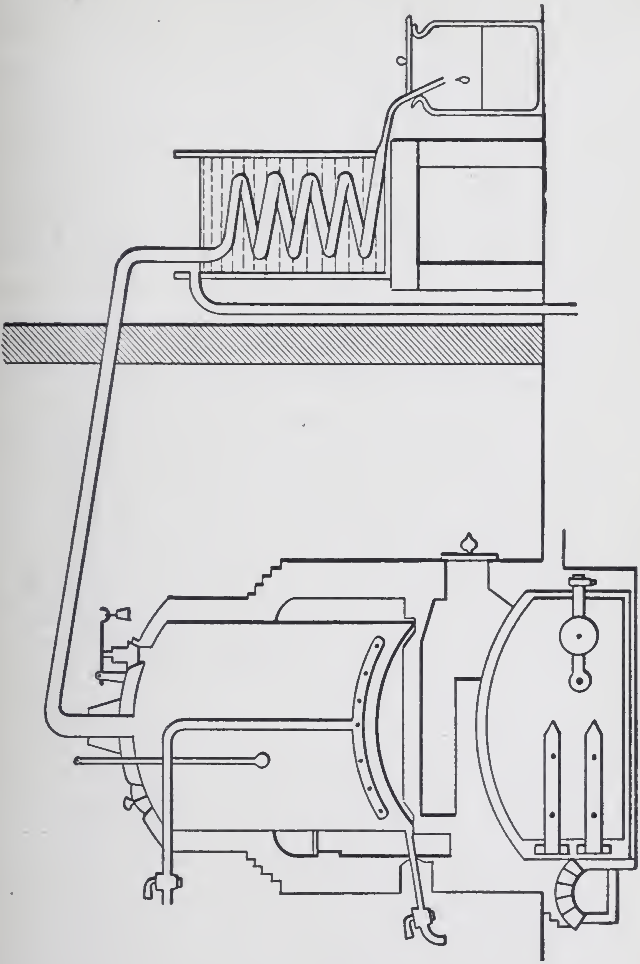

FIG. 41.—Tar Still.

fire is moderated to avoid frothing. The temperature is carefully watched by means of the thermometer and the distillate separated into the several fractions, the number of which varies with the tar. Usually the first fraction consists of the runnings of the still until they are free from water, shows a sp. gr. of 0.89 and is known as *"first runnings"* or *"light essences."* The fire under the still is moderated, the end of the condenser attached to a second receiver and the distillation continued till a sample just sinks in cold water—*light medium oils.* A third receiver collects the *"heavy oils,"* the distillation proceeding until a test solidifies in cold water (anthracene). These oils show a specific gravity of 0.99, and towards the end the water in the condenser is heated to 70° or 80° C. (158-176° F.) to prevent clogging. The fourth receiver is then put in connection, the fire increased, and the *"anthracene oils"* pass over. The residue left in the still after this is allowed to cool a little, and then run out into moulds, when it forms the *"pitch"* of commerce.

The various fractions are then rectified in separate stills, and are thus divided into the following portions:

(a) Light essences or first runnings yield—
  (1) Light naphtha.
  (2) Heavy naphtha.
  (3) Residue added to 13.
(b) Light or medium oils—
  (4) Light naphtha added to the light essences (a).
  (5) Heavy naphtha.
  (6) Light oil.
  (7) Carbolic oil mixed with the heavy oil (c).
(c) Heavy oil—
  (8) Light oils mixed with (b).
  (9) Carbolic oil.
  (10) Creasote oil.

(d) Anthracene oil—

 (11) Raw anthracene obtained by cooling and filtering; the filtrate, "green oil," is distilled and yields—
 (12) Light oil (until a test just sinks in water).
 (13) Creasote oil (until a test solidifies in cold water).
 (14) Residue of pitch.

(e) Pitch; as soft pitch is more valuable than hard, the residue of the latter is usually softened by adding to it some of the creasote oil or green oil, and is used for making asphalt, briquettes, etc.

The various fractions are further purified by treatment with sulphuric acid (to remove the anilines and other bases) and caustic soda (which removes the phenols, etc.), washed with water and again subjected to distillation.

PROPERTIES OF THE VARIOUS FRACTIONS.

Benzene, Toluene and Xylene.—The purified light essences are distilled in a retort provided with a "dephlegmating column," *i.e.,* an inverted condenser, which allows any liquid condensing at the temperature to which it is heated to fall back into the still. Thus if a mixture of three hydrocarbons, benzene, toluene and xylene be thus heated and the dephlegmating column be at 80° C. (176° F.) a benzene containing very little toluene and practically no xylene will pass over as a distillate. The temperature of the column is then raised, when toluene containing a little benzene and some xylene goes over. Sometimes the temperature of the column is allowed to still further increase, when xylene is obtained; more generally, however, the process is stopped after the toluene has come over. The residue in the still then forms the *solvent naphtha* or *tar spirit* of commerce.

The commercial products obtained from the light oils and essences are known as—

(1) *Benzene for Blue.*—This is nearly pure benzene; it boils at 80° C., but contains, in addition to benzene, thiophene and certain fatty hydrocarbons.

(2) *Benzene for Red.*—Three commercial products are classed under this name, 30% benzol, 50% benzol and 90% benzol. The percentages denote the amount of the substances which distils below 100° C. (212° F.). They are all mixtures of benzene, toluene, xylene, other hydrocarbons and thiophene.

PURE BENZENE OR BENZOL (C_6H_6).—Benzene, the simplest aromatic hydrocarbon, has a specific gravity of 0.885, boils at 80° C. (176° F.) and solidifies at 0° C. (32° F.), which latter property is employed to separate it from toluene. It is a mobile, colourless, and not unpleasant-smelling liquid, insoluble in water, dilute acids and alkalies, but miscible with nearly all volatile solvents.

It flashes below 0° C. (32° F.) and where its vapour is mixed with air forms an explosive mixture, the maximum explosive violence being obtained theoretically when the air contains 2-3% of the vapour.

Concentrated sulphuric acid attacks it, converting it into a sulphonic acid. Treated with nitric acid, nitrobenzene is formed.

Nitrobenzene, or *"oil of mirbane,"* is an almond-like-smelling yellowish liquid, and is largely used for scenting soaps ("old brown Windsor") and in the manufacture of aniline. In fact, the chief application of benzene is in the preparation of this substance, which serves as a starting-point in the preparation of the aniline colours.

Benzene forms an excellent solvent for fats, resins and many other kindred substances, and is on that account used in chemical cleaning, rubber industry, etc.

Benzene, C_6H_6, must not be confounded with benzine or benzoline or petroleum spirit, from which it is distinguished not only chemically, but in most of its physical properties. The following table will illustrate this—

BENZENE.	BENZINE.
Benzol, or coal-tar benzene.	Benzoline or petroleum spirit.
Boiling point, 80° C. (176° F.).	Wide range of boiling, 54-120° C. (130-248° F.).
Composition, C_6H_6.	Complex mixture of fatty hydrocarbons.
Carbon, 92.3%.	Carbon, average, 84%.
Specific gravity, 0.885.	Specific gravity, 0.69-0.73.
Dissolves iodine, forming violent solution.	Dissolves iodine, giving red solution.
Easily dissolves coal-tar pitch.	Will not dissolve coal-tar pitch.
Dissolves carbolic acid in all proportions.	Will not dissolve carbolic acid.
Dissolves alcohol in all proportion.	Will not dissolve alcohol save in proportions under 33%.
Treated with conc. nitric acid, with which it is miscible, gives almond-like odour and evolves much heat.	Will not mix with nitric acid and gives no almond smell.
	More inflammable than benzene.

TOLUENE, $C_6H_5CH_3$.—Similar to benzene, but has a higher boiling point, namely, 111° C. (232° F.). Sp. gr., 0.875. Used in the manufacture of coal-tar dyes, etc.

XYLENES, $C_6H_4(CH_3)_2$.—There are three of these substances known boiling at 138°, 139° and 141° C. (280°, 282° and 286° F. respectively).

SOLVENT NAPHTHA OR COAL-TAR SPIRIT.—The residue left in the stills after separating benzene and toluene from the higher boiling constituents of the light essences or oils forms, as already mentioned, the solvent naphtha or tar spirit of commerce. It consists of a mixture of the aromatic hydrocarbons, xylenes, mesitylene, pseudocumene, trimethyl-benzene, $C_6H_3(CH_3)_3$, boiling from 138-166°C. (280-330° F.), and other substances. Generally the boiling point of the solvent naphtha ranges from 130-180° C. (266-356° F.) and its specific gravity from 0.865-0.975. It forms a colourless or slightly yellow liquid (according to the quality), smelling like coal-tar. It is very inflammable, but not so much so as benzene, shale or petroleum naphtha; flashing at 100° F. In its other properties it closely resembles benzene and toluene, As an excellent solvent for fats, rubber and other resinous and oily materials, solvent naphtha is employed as a turpentine substitute in making cheap varnishes, and also finds application in chemical cleaning and as an illuminant. It is sometimes adulterated with shale naphtha, which lowers the fiash-point.

NAPHTHALENE, $C_{10}H_8$.—This hydrocarbon, which is frozen out of the heavy oils, is purified by pressing, distilling and recrystallising from naphtha, when it is obtained in white, pearly leaflets or tablets, melting at 80° C. (176° F.) and boiling at 217° C. (423° F.). Commercial naphthalene is often met with in blocks or cylinders, which are cast. It finds application in carburetting coal-gas ("albo-carbon" light), as a disinfectant, in the manufacture of dyestuffs, etc. Naphthalene is combustible, burning with a smoky luminous flame.

ANTHRACENE, $C_{14}H_{10}$.—A white, pearly substance with a beautiful bluish bloom, melts at 212° C. (415° F.) and distils at 360° C. (680° F.). Used in the manufacture of alizarine and in the manufacture of dyestuffs.

CARBOLIC ACID, mainly Phenol, C_6H_5OH.—The use of this substance as a disinfectant may be mentioned. It is obtained from the alkaline washing of the "carbolic oils," boiling between 150° and 220° C. (302-428° F.).

CREASOTE.—A thick, oily liquid, smelling strongly of coal-tar and containing a number of phenols, as carbolic acid, cresol, naphthol. It is largely used in preserving timber, etc. Wood creasote is a similar substance obtained from "wood-tar."

COAL-TAR DEAD OIL OR GREEN OIL.—Obtained, as already mentioned, as a by-product from the anthracene oils; is used as a fuel, as an illuminant in the "lucigen" or "Wells light," as an adulterant in making cheap wagon greases and for softening pitch.

CHAPTER XII.

PAINT AND VARNISH MAKING.

Linseed Oil—Oil "Boiling" and "Driers"—Pigments and Paints—Enamels—Anti-corrosive and Anti-fouling Compositions—Spirit and Oil Varnishes—India-Rubber and Gutta-Percha.

LINSEED OIL is almost the only oil that finds application in these industries, although some of the cheaper paints are adulterated with rosin oil. (See page 204.) It owes its preference to the fact that as a drying oil, when exposed to air in thin layers, it absorbs oxygen and becomes converted into a hard, transparent, leather-like substance —linoxyn. (For constants see table, page 158.)

By boiling linseed oil with certain substances, so that they become dissolved therein, it acquires the property of drying more rapidly when exposed to air. Such substances are known as driers, and are compounds of lead, or manganese. They are supposed to act as "carriers of oxygen," uniting with that element from the air and giving it up again to the oil, thus being reduced and again placed in the position to repeat the process. The commonest "driers" are the following:

(1) *Litharge, Oxide of Lead, PbO.*—This substance is readily dissolved in linseed oil; when heated therewith it forms a lead soap; 1-2% is usually employed.

(2) *Red Lead, Pb_3O_4.*—An oxide of lead, prepared by heating litharge in a current of air. It is less easily dissolved than the former, but is esteemed by some oil

boilers on account of its supposed hardening action on the oil. As it contains more oxygen than litharge (to which condition it must probably be reduced before it will dissolve), it also acts as an oxidising agent to the oil.

(3) *Sugar of Lead* or *Lead Acetate,* $Pb(C_2H_3O_2)_2.2H_2O$.—This substance melts at a low temperature in its water of crystallisation and is easily dissolved by linseed oil. During boiling acetic acid is expelled.

(4) *Black Manganese* or *Manganese Dioxide,* MnO_2, and *brown manganese* or *hydrated oxide of manganese,* $Mn_2O_3xH_2O$.—Both occur as minerals, but the former is also artificially obtained from Weldon still liquors (in the manufacture of bleaching powder). Manganese dioxide is dissolved by oil only with difficulty at a high temperature, but is a very powerful drier; ¼% is said to be sufficient to use. Brown manganese is more easily soluble, but the trade varieties differ very greatly in their ease of solution.

(5) *White Manganese, Manganese Sulphate,* $MnSO_4$.—A strong drier, but very difficult to dissolve.

(6) *Borate of Manganese* is of very variable composition. It is dissolved by even cold oil, although more easily by oil at 212° F. A very powerful drier.

(7) *Sulphate of Zinc,* $ZnSO_4$.—This substance is used by some oil boilers, but is of doubtful utility.

Other salts of lead and manganese have been introduced as driers, and their employment is said to present some advantages. They are, however, of little interest in this connection. It may be noted that "driers" also cause other drying and semi-drying oils to absorb oxygen more rapidly from the air, though few oils "dry" so well as linseed.

OIL BOILING.—Linseed oil is boiled with the following objects:

(1) To dissolve the driers therein.

(2) To coagulate and partly remove the mucilage.

(3) And often for the purpose of thickening it. Two processes are employed, namely, fire boiling, the older method, and steam boiling, of more recent introduction.

FIRE BOILING.—The oil is heated in a large iron boiler, which should only be two-thirds full, over a fire. The fireplace is generally situated outside the shed so as to avoid as much as possible any risk of ignition if the oil boils over. The firing is so conducted that the temperature of the oil rises to 500° F. in 2 hours, at which temperature it is maintained for some 2 hours, during which the driers are gradually added. The boilers are provided with mechanical agitators and contain from 100 to 600 gallons. When the operation is complete, *i.e.,* after 5 to 6 hours, the oil is left to cool over night and is then pumped out into the storage tanks. The sediment in the boiler, "boiled oil foots," is employed in making putty, etc.

As the temperature rises the mucilaginous and albumenous matters in the oil are coagulated and rise to the surface as a froth or scum. If the oil be newly pressed or unrefined, either by tanking or "chemicals," the mucilage, together with the contained water, may cause so great a formation of froth that the oil, if carelessly heated, will boil over. This danger presents itself chiefly during the preliminary heating. When 400° F. or so is reached the oil begins to give off very irritating vapours, "acrolein," formed by the partial decomposition of the glycerides. In adding the driers, too much should not be added at once, for their vigorous action may cause the oil to boil over. It may be noted that it is the solution of the driers that causes the oil to dry and not the mere boiling.

Boiled oil is distinguished from raw oil in its oxygen absorption, viscosity, specific gravity (0.940-0.950), odour, taste and colour. The latter varies from light brown to dark red brown, according to the driers used, the temperature and method of boiling and the quality of the oil. Boiled oil, like raw oil, is miscible with nearly all the volatile solvents.

STEAM BOILING.—As already mentioned, some of the driers are soluble at a much lower temperature than others, consequently attempts have been made to prepare a drying linseed oil by heating the oil with driers at a steam heat. Such an oil will dry well enough, but is deficient in viscosity and therefore unsuitable for many purposes. By heating the oil in a closed, steam-jacketed vessel and agitating it, air being blown through, it is possible to correct this, and an oil of any viscosity may be obtained.

Steam-boiled oil is paler in colour than fire-boiled and more viscous. It dries, too, equally as well if suitable driers be employed.

Many modifications of the above methods, such as boiling by superheated steam, are in use.

Boiled linseed oil prepared by either of the above processes is an avid absorber of oxygen. When exposed to air it gains 14-16% in weight, and consequently evolves a large amount of heat during the process. Cotton waste or other fibrous or porous combustible material soaked in boiled linseed oil very rapidly inflames, especially if stored in bulk. If dissolved in turpentine, as in paints and varnishes, and spread on cotton the rapidity of absorption and consequently the rise in temperature is greater still.

PIGMENTS AND PAINTS.

In the manufacture of paints certain coloured powders or pigments are mixed or ground with some vehicle, generally raw or boiled linseed oil, and thinned with a mixture of raw and boiled oil and turpentine or one of its substitutes.

Only those pigments which increase the drying of raw linseed oil are of interest to us, and they are—

WHITE LEAD.—A mixture of hydrate and carbonate of lead in varying proportions, sometimes corresponding to the formula $2\ PbCO_3, Pb(OH)_2$. The more hydrate of lead, $Pb(OH)_2$, the pigment contains the greater is its drying power. White lead is the most largely used of all pigments, forming a "base" in most paints. It is esteemed on account of the preservative action it exerts on the objects painted.

RED LEAD. (See driers.)—Largely used as a protective for coating iron, etc.

LEMON AND ORANGE CHROMES.—These two pigments, especially the latter, act as driers when mixed with raw oil; they are the commonest yellow pigments.

BRUNSWICK GREENS.—Mixtures of lemon chromes with Prussian blue and more or less barytes. They exert a slight drying action on oil and are by far the most commonly employed of all the greens.

Natural oxides of iron (rouge, etc.) ochres, siennas and umbers (especially these) exert more or less drying action on oils in virtue of the small quantities of manganese they contain.

Many of the lakes are made from the artificial and natural colouring matters and lead acetate, litharge or red lead, and consequently act as powerful driers.

Some of the pigments made from organic substances, as Prussian blues, carbon and vegetable blacks and many of the above mentioned lakes, are very inflammable when distributed in fine dust or ground with an oxidising substance in a dry state. There is a case on record* of a cask

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* *Jl. Soc. Chem. Indus.*, 1895, p. 947.

of red made from eosine and red lead taking fire. The cause was traced to a gas jet igniting the fine dust raised on opening the cask and the fire spreading to the bulk in the cask, the combustion was there maintained at the expense of the oxygen contained in the red lead.

LAMPBLACK. (See carbon, Chap. V.)—This pigment often contains unburnt oil which, if of a drying nature, may absorb oxygen and give rise to spontaneous combustion. There are several cases on record where casks of this pigment on standing have grown almost red hot inside.

In preparing paints, the pigment is first mixed with the oil, generally raw oil, and then the mixture made more perfect by grinding. To the resultant paste, boiled and raw linseed oil and turpentine are added to thin it. The former, boiled oil, is not used alone, for it is apt to cause the paint to crack, and consequently, in order to make the mixture dry quickly enough, it is necessary to add some drier for the raw oil. This is especially the case where a non-drying pigment is used. The drier (paste drier) usually consists of one or more of the oil driers previously described, mixed with barytes, white lead, whiting, etc., and oil.

Turpentine serves to make the paint thinner, so that it works better under the brush and also to increase the rapidity of drying.

In the use of paints the same precautions have to be observed as with drying oils, great care being taken, for example, not to leave cotton waste or cloths used for cleaning brushes, etc., lying about; only here the risks are even greater, for not only does paint contain a drying oil, but one charged with a drier and turpentine. So that it oxidises with great facility.

ENAMEL PAINTS consist of some pigment, often zinc white, ground with a varnish which may be either an oil or a spirit varnish, or a mixture of the two.

ANTI-CORROSIVE AND ANTI-FOULING COMPOSITIONS are now largely employed for painting ships' bottoms and other submerged iron or woodwork to prevent corrosion or incrustation. They vary very greatly, but generally consist of some fat, resin or pitch, pigment (often oxide of iron or red lead) and a volatile solvent, such as naphtha (coal-tar or shale), turpentine or petroleum spirit. These volatile solvents constitute the chief danger in their use, and the many accidents resulting in dangerous fires and loss of life have led to the placing of restrictions on their employment and transport by the government. (See Chap. XIV.)

VARNISHES

are of two kinds—spirit varnishes and oil varnishes.

SPIRIT VARNISHES are made by dissolving certain resins in methylated spirit or other volatile solvent. The *modus operandi* is in general to leave the powdered gum or resin in a warm place, in contact with the solvent, for some time and occasionally shake or otherwise agitate the mixture, or the resin is dissolved in a still provided with an inverted condenser. The resins used in the manufacture of spirit varnishes are chiefly shellac, rosin, Manila copal, gum sandarac, mastic and melted resins. Spirit varnishes find application for paper and wood or wherever a quick drying varnish is essential.

OIL VARNISHES.—In the manufacture of these the resins, such as copal, kauri, dammar, asphaltum, etc., are melted in a copper pot and the product dissolved in hot linseed oil which has previously been boiled with the addition of driers. The solution thus obtained, is then poured into turpentine or a substitute, great care being taken to conduct the operation at a distance from any free fire or flame, as much inflammable vapour, which is heavy and travels along the ground, is evolved during the mixing. If a fire occurs, sand is the best extinguisher.

Oil varnishes are the most commonly used of all; they are generally employed for varnishing already painted objects or objects with smooth surfaces, as in coach varnish, japans, etc.

The fire risks are the same as those of their constituents, boiled linseed oil and a volatile solvent.

INDIA-RUBBER AND GUTTA-PERCHA.

India-Rubber or caoutchouc is the solidified milky sap of many trees belonging to various families, as Siphonia, Hevea, Urcea, Ficus, Papaver, growing in South America, the Malay Archipelago and parts of Asia and Africa. Incisions are made in the stems of the trees, small dishes of unburnt clay attached and the sap collected. These dishes are coated all over with the sap and dried in the smoke from the burning nuts of urucury palm (*Attalea excelsa*), etc., when the sap is changed into a dark brown, sticky mass. The "forms" are broken when the drying is complete, the clay shaken out and the crude rubber, after washing in water, is sent into the market.

At Para, in Brazil, the sap is dried on paddles or spoon-shaped pieces of wood in the smoke of the urucury nut, but in some parts of Brazil the smoke-drying process is neglected and the rubber precipitated from the sap by alum solution.

Pure rubber is, when seen in thin layers, white and transparent; it is tasteless, almost without smell and extremely elastic. When two freshly cut surfaces are pressed together they adhere firmly. At about 125° C. (257° F.) rubber melts to a tarry, tough liquid which never again acquires the properties of raw rubber. On further heating decomposition takes place and an ethereal oil distils over. At temperatures below the melting point rubber merely softens with heat.

Chemically, rubber is a mixture of two hydrocarbons, showing on analysis the following compositions:

Carbon	87.3
Hydrogen	12.7
	100.0

It burns in air with a smoky, luminous flame, is not easily attacked by acids or alkalies and has a sp. gr. of 0.925. In ether or benzine (petroleum naphtha) rubber swells to 30 or 40 times its volume. It is insoluble in alcohol, but dissolved by benzene, turpentine or carbon disulphide more or less easily.

GUTTA-PERCHA, the solidified sap of the East Indian gum tree.—The mode of collecting it is similar to that employed for rubber. The sap is sun-dried and the crude gutta comes into the market in the form of leathery sticks or cakes of a dark brown colour, sp. gr. 0.979. It is very tough at the ordinary temperature, but soft and plastic in warm water, when it can be moulded into any desired form. When heated to higher temperatures gutta-percha behaves like india-rubber, as it does towards solvents, acids and alkalies. Chemically, gutta-percha consists of about 80% of a hydrocarbon similar to those in rubber, 15% of albumen and 5% of essential oil.

Gutta-percha absorbs oxygen from the air, forming a powdery, yellow substance. On account of its great resistance to acids and alkalies it is used for making battery cells, bottles or other vessels to contain hydrofluoric acid or soluble fluorides. Like rubber, it is a non-conductor of electricity, and is largely employed for coating wires, etc., as an insulator.

Uses of Rubber.—If rubber be heated to about 280° F. with sulphur, or if it be treated with a cold solution of sulphur chloride in carbon disulphide, benzene, etc., it is converted into a grey mass, which does not become sticky on heating, is firmer and retains much of the elasticity and resiliency of rubber. These facts are made use of in the arts and upon them are based two processes of "vulcanising" rubber, the hot and cold vulcanisation methods. For details of these processes the reader is referred to the excellent article on india-rubber in Thorpe's Dictionary of Applied Chemistry.

When such inflammable materials as benzene, benzine or carbon disulphide are employed in an industry great care must, of course, be taken to avoid approaching any vessel or substance containing them with a flame; whenever practicable, electric light should be used as an illuminant.

Rubber is used in the manufacture of water-proof goods, of mats, tubing, packing, in the insulation of wire for electrical purposes, generally in the vulcanised or partially vulcanised form.

Vulcanite and ebonite consist of a mixture of rubber, sulphur and gutta-percha, with the addition of more or less pigment. Vulcanite contains from 20% to 30% of sulphur, while ebonite may contain as much as 60%.

Rubber Substitutes.—Many attempts have been made to manufacture a substitute for rubber, and there are such materials on the market. They consist, for the most part, of some fatty oil combined with sulphur, and mixed with various gums, resins and pitches. Although some of them possess the resilience of rubber, they are all inferior to it in many respects.

CHAPTER XIII.

TEXTILE MANUFACTURES.

Cotton, Flax, Jute, China Grass, Silk, Wool—The Preparation of these Fibres, by Scouring and Bleaching, for Spinning and Dyeing—Silk Weighting—Dyeing—Dyestuffs, and the Principles of their Application, Mordants—Aniline Black Dyeing and Printing, Nitro Colours, Dangerous Materials Used in these Industries.

It is the intention of the authors to give in this place merely a brief outline of the principal operations to which the various textile fibres are subjected in their preparation for spinning, weaving and dyeing. Only those processes can be dealt with which involve the use of chemical reagents or which appear from other causes to present fire risks. Details cannot be given, nor can the purely mechanical operations of carding, combing, spinning, etc., be entered into, but it may be noted that during many of these operations the material is spread out loosely and if once ignited is very difficult to extinguish. If any hard or gritty particles of foreign matter find their way into the quick-running machinery the friction may produce sparks, when ignition of the textile fibre is almost certain to take place. This is especially the case in such operation as rag grinding, where bits of iron, buttons, etc., may cause fire in this way. Consequently many rag grinders have a steam-pipe attached to the machine, so that if fire through friction arises it may at once be extinguished by turning on the steam, which quickly fills the interior of the machine and excludes the air.

Cotton.—The fibre of the downy envelope of the seeds of various species of the cotton plant. Chemically, cotton consists essentially of cellulose, $C_6H_{10}O_5$, a substance related to starch and dextrine, but contains in addition about 5% of other substances, known under the name of pectic matter.

If heated to 230° C. (446° F.) it turns brown and begins to decompose. In contact with air it burns without emitting any very strong odour but with a luminous flame, being by far the most combustible of the textile materials.

Cotton is not dissolved by any of the ordinary solvents. Nitric acid converts it into cellulose nitrate. (See gun-cotton.) Sulphuric acid changes it into a parchment-like substance, amyloid, or into dextrine, according to conditions. Concentrated hydrochloric acid, or the gas, produces a powdery substance.

The action of sulphuric acid or hydrochloric acid upon cotton fibre is utilised in the preparation of extract wool from union rags (which see).

Caustic alkalies convert cotton into "oxy-cellulose" and are employed in the "mercerisation" of cotton, a process used very largely at present for imparting a silk-like gloss to cotton goods.

Cotton Bleaching.—Before dyeing, the pectic and other impurities must be removed from cotton. This is done by subjecting the raw material, either as yarn or in the woven form, to the action of the following baths—

(a) Hot dilute carbonate or hydrate of soda ("Lye boil").

(b) Dilute solution of bleaching powder ("Chemicking").

(c) Dilute sulphuric acid ("Souring").

(d) Washing with water.

If the calico has to be kept white, or dyed with light shades or with Turkey red, the operations are more elaborate.

When calico is to be printed it is also necessary to remove all the "fluff" or loose fibre from its surface, and this is done by passing the goods through a "singeing machine," of which there are four varieties in use—

(1) *Plate Machines.*—Here the calico is rapidly moved over the surface of a plate heated to redness, and is then immediately passed through damping rollers, which extinguish any sparks carried along with the cloth.

(2) *Coke Machines.*—A brightly burning, smokeless, flameless fire takes the place of the hot plate.

(3) *Roller Machines.*—In this form the flames of the fire are sent through revolving copper rollers, between which the cloth passes.

(4) *Gas Machines.*—The cloth in open width passes rapidly over a row of small non-luminous gas flames, which may be moved into any position by levers.

The first machine is used for thick goods, while the fourth is most useful for thin.

FLAX, JUTE OR CHINA GRASS.—These fibres are derived from the stems and leaves of several plants. Flax is yielded by the linen plant, *Linum usitatissimum;* jute, by various species of *corchous* cultivated in Bengal, and china grass by a member of the nettle family, *Urtica nivea,* growing in China, Japan and the East.

All these fibres are obtained from the plants by a process known as "retting." The plants are first stripped of the seeds and then packed in crates and placed in tanks or ponds of water. The pectic or resinous matters forming the plant juice ferment, and so the fibres are loosened, not only from each other, but also from the woody stem of the plant. When the retting is complete the plants are removed and dried. The next operation consists in "breaking," which is accomplished by passing the retted plants through fluted rollers whereby the woody stem is removed from the fibre proper. Further separation of the fibres is effected by "hackling," a kind of combing operation dividing the fibres into long and short ones.

Chemically, flax, jute and china grass consist of cellulose, but in the crude state contains varying amounts of other substances, pectic matters and gum. As such, their behaviour toward various agencies is similar to cotton. Flax contains 15-25% pectin; jute, 2-8%. These impurities are removed during bleaching, which is carried out similarly to cotton bleaching, only with jute, sodium bisulphite, or hypochlorite, is used in preference to bleaching powder.

WOOL.—Wool is less susceptible to chemical reagents than are the vegetable fibres. Acids, if dilute, exert little or no action, but if concentrated, mineral acids cause wool to disintegrate. Nitric acid converts it into a yellow substance, the so-called "xanthoproteic acid." Sulphurous acid or sulphud dioxide bleaches wool by removing any yellow tint. Concentrated sulphuric acid, on long standing, dissolves wool, which is reprecipitated by the addition of water.

On the other hand, wool is very susceptible to the action of alkaline solutions, being completely dissolved by hot caustic soda or potash, from which solutions the addition of a dilute acid precipitates it as an amorphous powder. Dilute ammonia water and alkaline carbonates have little or no action. Bleaching powder or chlorine acts very energetically on wool, and hence cannot be used as bleaching agents.

Chemically, wool consists of a complex nitrogenous organic substance, *i.e.,* contains nitrogen in addition to carbon, hydrogen and oxygen, some sulphur is also present. It is less combustible than the vegetable fibres, although it will burn when ignited, leaving a cindery residue of carbon and evolving a very characteristic odour. When heated, ammonia is evolved.

Raw wool contains, in addition to the wool proper, quantities of fatty matter and potassium salts ("yolk") derived from the perspiration of the sheep. Before dyeing or bleaching this fatty matter must be removed, and this is done by—

SCOURING.—The methods in use may be divided into two classes—

(a) *Scouring with Alkaline Solutions.*—The loose wool is first worked in warm water, which dissolves the potassium salts of the "yolk," and emulsifies some of the fat. It is then removed to another tank, where it is worked either by hand or machine in an alkaline solution at about 120° F. The alkaline solutions may be "lant" or stale urine, sodium carbonate solution (1-2° Tw.) or soap. After a short time it is taken out, placed on a screen to drain and washed in a wool washing machine.

(b) *Scouring with Volatile Solvents.*—Many attempts have been made to remove the wool fat by other solvents than alkaline solutions, but have not led to the general introduction of this process. According to this method, the raw wool is treated with benzene, carbon disulphide, fusel oil or petroleum spirit, which dissolves the wool fat, but not the potassium salts (wool perspiration), which latter are, however, dissolved by after treatment with water. Many machines have been devised, among which may be mentioned those of De Heyl, Van Haecht, Mullings, Singer and Burnell. It is claimed that wool scoured in this way is superior to alkaline scoured wool, the alkali tending to injure the fibre. The use of volatile solvents, which are mostly very inflammable and hence dangerous, and the expense of the plant and recovery of the solvent, have doubtless prevented the general adoption of this method.

YARN AND CLOTH are likewise scoured with carbonate of soda or soap to remove the oils used in spinning (see cloth oils), for otherwise they could not be evenly dyed. Yarns are generally hung over wooden rods and worked by hand in the scouring liquor, or the hanks are linked together and passed in chain form through the scouring tanks, and then through squeezing rollers. Woollen cloth is scoured in open width in specially constructed machines.

WOOL BLEACHING.—Only when wool is to be used for white goods or those which have to be dyed with very delicate colours is it bleached.

(a) *Gas Bleaching, Sulphuring, or Stoving.*—This is the most commonly used of the methods of bleaching wool. After scouring and washing the goods are hung in a brick chamber, which can be filled with sulphur dioxide. When the goods are in the chamber the stove containing the necessary amount of sulphur (6-8% of the wool present) is ignited, the door of the chamber shut and the moist goods are thus subjected to the action of the sulphurous acid formed for 6-12 hours. They are removed and well washed with dilute soda. If the goods are thin the operation is made continuous, the cloth passing through the stove over rollers, and out again backwards and forwards, until bleached. It may be noted here that if the goods are spotted with oil, the sulphur dioxide will react therewith, producing sulphuric acid, which will char the fibre in those places.

(b) *Liquid Bleaching.*—Two methods are in use—

(1) *Bleaching with Sodium Bisulphite.*—The goods, generally yarns, are worked in a solution of this substance and then in dilute sulphuric acid, washed with dilute soda and water and dried. The sulphuric acid liberates sulphur dioxide within the fibre, which attacks and destroys the colouring matters in the wool.

(2) *Bleaching with Hydrogen Peroxide.*—The substance itself is too expensive, but sodium peroxide, a convenient source of it, is now fairly cheap. When this body is added to water sodium hydrate and hydrogen peroxide are formed; the latter oxidises and destroys the colouring matter. The former, sodium hydrate, is apt to injure the wool, and consequently magnesium sulphate or Epsom salts is sometimes added to prevent this. The bleach obtained by hydrogen peroxide is much more permanent than that from sulphur dioxide. Sodium peroxide must be very carefully handled, as it evolves great heat when mixed with water and is such a powerful oxidising agent that, if it come in contact with anything inflammable or easily oxidisable, it may cause ignition. For instance, a mixture of sodium hydroxide and calcium carbide spontaneously inflames on contact with water.

Extract Wool.—In preparing union rags for pulling or grinding the cotton is usually first removed. Advantage is taken of the destruction which cotton undergoes when heated with mineral acids, while wool is very little affected. The processes of "carbonising," as they are called, are of two kinds, the older, Wet Method, and the newer, Dry or Gas Carbonising.

Wet Method.—The rags are steeped in dilute sulphuric acid, wrung out, and then heated in a chamber at 110° C. (230° F.), when the cotton or other vegetable fibre (cellulose) is so tendered that on removing it may be shaken out from the wool in fine dust. This method is also used for removing "burrs," which are generally of vegetable origin, from woollen goods.

Gas Carbonising.—Hydrochloric acid gas is now very generally employed for removing cotton from wool. After washing and drying the rags are heated in a gas-tight chamber and hydrochloric acid gas passed in. This process is free from danger, as the gas is a non-supporter of combustion.

NOTE.—In shaking the rags after carbonising, the dust being inflammable may give rise to dust explosions and hence fire. Where this process is carried out, the use of naked flames is to be avoided.

SILK.—The essential ingredient of silk is known as fibroin, a nitrogenous substance, but there are present in addition, quantities of silk glue or sericine, gelatine and albumen.

Concentrated mineral acids rapidly destroy silk, but when dilute have little or no action thereon. Strong caustic alkalies, as soda or potash, dissolve silk, but weaker solutions have little action, save that they remove the silk glue. Alkaline carbonates behave less energetically. Silk is less inflammable than cotton, but more so than wool; when heated or burning it emits a characteristic smell.

Silk is scoured and bleached before dyeing. The former process consists in treating the raw silk with hot soap solution ("boiling off") and then washing it with water, which is followed by the operations of stretching and "lustring." The bleaching process is similar to that used for cotton. *Souple silk* is silk which has only been partially scoured (degummed) and then treated with cream of tartar.

Silk Weighting.—Silk may be caused to swell and increase in weight when treated with certain solutions. This property is largely made use of by manufacturers, and has given rise to the process of "silk weighting." The substances employed as weighting agents are sugar; tannic acid; tannates of tin, aluminium, iron and gelatine; sulphates of lead and barium; phosphates, silicates and tungstate of iron; Prussian blue; catechu, etc., often prepared on the fibre by double decomposition.

According to J. Carter Bell, heavily weighted silks are liable to spontaneous combustion. Thus, a black silk, weighted up to 300-400%, took fire when heated to 230° F., and he states that such goods should not be packed close in large quantities. In 1871, a fire which occurred in an American silk-dyeing establishment, and some years ago another large fire in a Paris silk warehouse, were both attributed to the spontaneous combustion of heavily weighted silks. The true explanation of such spontaneous ignition is yet to seek.* It must be remembered that the tannins usually employed for blacks in conjunction with salts of iron, are very susceptible to oxidation, even absorbing oxygen from the air, and that heat thus engendered may cause ignition. This absorption is rendered more rapid in presence of alkalies, and consequently black silks which have been soaped would be most dangerous, the fatty acids of

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* *Jl. Soc. Chem. Indus.*, 1897, p. 303.

the soap also helping the heat formation by their oxidation. If lead salts have been employed as weighting agents, the lead, by acting as a dryer to the oils of the soap, and as a carrier of oxygen to the tannin, may increase the liability to fire. Over-dried weighted goods are especially liable to such ignition.

ARTIFICIAL SILK.—Of recent years many attempts have been made, with more or less success, to prepare, artificially, a fibre which will resemble silk in its gloss, feel, etc. The raw material for this manufacture has been for the most part cotton or some form of cellulose.

The most successful method up to the present consists in converting the cellulose into cellulose nitrate by means of sulphuric and nitric acids (see guncotton), dissolving the product in a mixture of ether and alcohol and forcing the thick solution (collodion) through fine glass jets. The threads thus obtained are freed from the ether and alcohol, used as solvents, by drying in a warm room, and as in that form they are very inflammable and explosive, the nitrocellulose is decomposed by treatment with alkaline sulphide solutions. If the denitration is properly carried out the thread now consists of cellulose only and is not more inflammable or dangerous than cotton, being, in fact, identical in composition with that substance. The process of manufacture is, of course, a dangerous one and great care has to be exercised throughout. Large quantities of artificial silk prepared by the nitro-cellulose method at Besançon, in France, are now imported into this country.

Cellulose is also soluble in zinc chloride solutions, and has been used in that condition for making artificial silk. Silk made from *cellulose thiocarbonate* or *viscose** has likewise been patented. These processes (especially the former) are less dangerous than the nitro-cellulose

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* See under Carbon Disulphide in Chap. XI.

methods, but the authors do not know if they are being worked commercially. Another method of imparting to cellulose a silk-like gloss is the "mercerisation" process, already mentioned under cotton.

Quite recently a method of preparing artificial silk from gelatine has been patented, and a small factory started in Glasgow, for its production. The material has the gloss and appearance of silk, and if the inventor succeeds in rendering it quite resistant to moisture it will probably find useful applications.*

DYEING.

Dyestuffs may be divided into two great classes, namely, those which dye the fibre directly without any previous treatment, consequently known as Direct Dyeing or Substantive Colours, and those which are only absorbed by the fibre after it has been treated with certain substances called mordants, and therefore designated Mordant or Adjective Colours. The various textile materials show a different attraction or absorptive power for colouring matters. Thus some dyestuffs are absorbed and retained by an unmordanted wool or silk, as magenta and many other coal-tar colours, and hence act as substantive colours thereto, while raw or unmordanted cotton or linen cannot be thus dyed; therefore those colours behave to the vegetable fibres as adjective colours. Hence the classification is not an exact one, but it may be noted that generally, if a dyestuff be substantive to cotton, it is usually substantive to wool, and if adjective to wool it is often adjective to cotton, and that wool and silk show a much greater attraction for dyestuffs than cotton or other vegetable fibres.

MORDANTING has for its object the fixing in the fibre

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* *Jl. Soc. Chem. Indus.*, 1899, p. 16.

of certain acids or bases which will unite with the dyestuffs (which are basic and acid respectively), and, by forming colour lakes therewith during the dyeing, will fix and render them "fast" to washing, etc.

As mordants for the dyestuffs of an acidic nature, salts of iron, aluminium, chromium, tin and lead are most generally used, while for basic colours tannic acid, sulphur and oil (olive or Turkey red oil and soaps) find application. The material, cotton, silk or wool, is worked in a bath containing one or more of the above substances in solution at a suitable temperature, wrung out, and then if necessary the mordant taken up is fixed in the fibre by treatment with some fixing agent, as ammonia, arsenite, carbonate, phosphate or hydrate of soda, or tartar emetic (fixing agents are most commonly employed with cotton), and the fibre or yarn is washed to remove excess of the mordant.

DYEING.—After mordanting the goods are brought into the dye-bath, which contains a solution of the dyestuff to which, if necessary, certain "assistants," as Glauber salts (sulphate of soda), soap, tartaric or sulphuric acid, etc., have been added, heated therein for some time and finally washed and dried.

In dyeing with substantive colours, the fabric without mordanting is "wetted out," *i.e.*, soaked in water, and introduced directly into the dye-bath.

Few of the dyeing operations themselves have any interest to us, but as the drying of dyed goods may present dangers, the methods in use will be briefly considered here.

Several types of drying machines are employed in works—

(a) Drying Loose or Unspun Wool, Silk or Cotton. The material after dyeing is placed on the surface of a galvanised iron network, heated underneath by steam-pipes, and having, likewise underneath, a fan arrangement which causes a current of hot air to pass through the material. Or the loose fibres are passed on endless bands through a steam-heated chamber. Wool is more commonly dried in the loose form than cotton.

(b) Yarns are generally dried in stoves or in the open air on poles.

(c) Cloth Drying.—The goods are dried either in stoves (calico) or on steam cylinders (calico and woollen goods), in hot-air chambers (calico) or on the tentering machine (woollen goods).

The Steam Cylinder Drying Machine consists of a number of hollow copper or galvanised-iron cylinders through which steam is passed. The cylinders are arranged in two horizontal rows and are caused to rotate by an engine and suitable gearing; the cloth in open width passes in loops, zigzag fashion, through the machine over these heated cylinders.

Tentering Machines.—To prevent shrinkage woollen cloth is generally dried on this machine. One of the commonest forms consists of a series of steam-pipes and endless chains, provided with points which penetrate the selvedges of the cloth, arranged in horizontal rows, so that the cloth in a stretched condition passes in horizontal zigzags through the heated chamber.

Sometimes heated air obtained from the waste heat of the chimneys is used instead of the steam-pipes.

SPECIAL DYEING PROCESSES.

(1) *Turkey Red Dyeing.* (See oils, Chap. X.)

(2) *Aniline Black Dyeing.*

This dyestuff is not a commercial article, but is prepared on the fibre by the dyer himself. The formation depends on the property, which some salts of aniline possess, of oxidising when in contact with certain oxidising agents to form a black powder of very complex composition. There are two varieties of aniline black which depend for their production on the method and vigour of the oxidation—a *blue black,* very susceptible to the action of acids or reducing agents, turning green, and a *violet black,* a more oxidised product, very fast to acids, alkalies, light, etc., not turning green, hence often termed "ungreenable" aniline black.

COTTON.—Aniline black is more often dyed on cotton than on the other fibres. Yarns and pieces are dyed by working them in a solution containing aniline hydrochlorate or sulphate, free hydrochloric or sulphuric acid and an oxidising agent, generally potassium bichromate. The goods are entered in the cold and worked for some time, then the temperature is gradually raised to 50-60° C. (120-140° F.), and the dyeing continued until complete.

A cold method is adopted in many works, using more of the oxidising agent and acid and generally some ferrous sulphate. After dyeing, the usual washing and soaping operations follow, and also a treatment with dilute sodium carbonate.

In *calico printing* the conditions for the production of an aniline black are very different to those described. Here a solution must be employed which only yields a black when subjected to some after treatment, for if a solution containing already formed aniline black (an insoluble substance) in suspension, be printed on the fabric no fixation takes place, and the resultant black is not fast to washing. The black must therefore be produced on and in the fibre itself, and this is effected in various ways, but in all cases the "ageing" process, *i.e.,* exposure of the printed goods to air in a heated chamber, is employed. Briefly the operations are as follows: A mixture of aniline oil, hydrochloric acid, a copper salt, sodium or potassium chlorate and ammonium chloride, with or without the addition of a thickening of starch paste, etc., is made, care being taken to avoid excess of acid, and the calico is padded or printed with the mixture. The fabric is then suspended in a moist atmosphere in a room heated to 30-38° C. (86-100° F.) for some time for the black to develop, then removed, passed through dilute solutions of potassium bichromate and sulphuric acid, washed, soaped and finally dried.

The copper sulphate or chloride, the salts usually employed, unfortunately attacks the iron work of the machines ("steel doctors," etc.) and, as acid salts, tender the fibre. Various attempts have been made, with more or less success, to replace them by other oxidising agents free from these faults. Thus, precipitated copper sulphide (CuS), an insoluble substance, and consequently incapable of causing corrosion, mixed with aniline, hydrochloric acid, sodium chlorate and a thickening agent, has been used. No corrosion of the iron work takes place, and in the ageing room the sulphide is oxidised to sulphate, producing a good black.

Potassium and ammonium ferro-, and ferricyanides, vanadium salts, copper sulpho-cyanide, etc., have also been used, but the black obtained by the aid of these substances has objectionable characteristics.

The tendering action of copper sulphate (due to the liberation of sulphuric acid) on the cotton is said to be avoided by adding to the mixture an equivalent quantity of aluminium acetate. Aluminium sulphate and free acetic acid are formed, which have no action on the cotton, the acid being expelled during ageing.

The chemical changes taking place during the formation of aniline black are very complex and but little understood. Aniline, $C_6H_5NH_2$, parts with some of its hydrogen by oxidation to form aniline black, which has the empirical formula C_6H_5N. The removal of the hydrogen is effected by the combined oxidising action of the sodium or potassium chlorate and the copper salt. The cupric salt (chloride) appears to be reduced by the aniline to a lower state of oxidation—cuprous chloride; and again oxidised by the chlorate to cupric chloride, and again reduced, and so on, the copper thus serving as a carrier of oxygen from the chlorate to the aniline. When copper sulphate is employed, chloride is formed by interchange with the aniline hydrochloride or other chloride present. If copper sulphide be used it is first oxidised to sulphate and then behaves as above. Ferrocyanides of potassium and ammonium act similarly, being oxidised to ferricyanide by the chlorate, and reduced by the aniline, acting as carriers of oxygen.

The dangers of fire during the dyeing of aniline black may be thus summarised—(1) Those arising from the employment of chlorates. The general properties of these substances have already found mention, but it may be noted that chlorates when treated with acids liberate chloric acid, which is decomposed by heat into chlorine peroxide, ClO_2, a very explosive and powerful oxidising substance. The presence of much *free* hydrochloric or sulphuric acid in the aniline black printing mixture should therefore be avoided, if only for this reason. (2) Such easily oxidisable substances as aniline, and, where it is employed, copper sulphide, and the presence of oxidising agents on the padded calico render its storage before ageing dangerous, for the heat produced by the chemical reactions which take place may prove sufficient to cause inflammation. After ageing and washing there is, of course, no such danger.

Probably the greatest danger in connection with aniline black dyeing is the danger of the oxidation processes, which are essential to the production of the colour, going on where the dyed material is piled together in heaps. Under these conditions the heat evolved cannot escape freely, consequently a high temperature is quickly attained and inflammation commences. This risk is greatest when the goods are just removed from the "ageing" chamber, and if they then, without washing, be piled up closely and left undisturbed, heating is sure to take place in a short time and actual ignition may occur. The precaution to be employed in order to obviate the danger is to keep the goods loose and freely exposed to the air for some time after "ageing," so that the heat which is evolved by the oxidation processes may be dissipated and dangerous temperatures thus avoided.

Aluminium chlorate is sometimes used instead of the sodium or potassium salts, and probably acts more energetically.

Wool and silk are rarely dyed with aniline black. According to a recent patent, however, loose wool may be dyed by soaking it in the usual solutions and exposing to air in a wire gauze, rotating, cylindrical drum in a chamber heated to 30-35° C. (86-95° F.).

(3) *Nitro-Colouring Matters.*—Several Nitro-compounds, derived chiefly from phenol (carbolic acid) or naphthol, have found applications in dyeing wool and silk. Under certain conditions they are explosive.

Picric Acid, tri-nitro-phenol, $C_6H_2(NO_2)_3OH$.—Obtained by the action of a mixture of nitric and sulphuric acids on phenol (carbolic acid, C_6H_5OH), besides being used as an explosive (which see), also finds limited application in wool and silk dyeing for producing a lemon yellow.

Wool is dyed at 60-100° C. (140-212° F.) in a bath containing 1-4% of the colour and 2-4% of sulphuric acid. The result is not fast to soap or milling, changing to brown under the influence of alkalies.

Silk, for which picric acid is more largely used, is dyed in the same way. Weighted yellow silks were formerly obtained by mordanting the goods with lead acetate and then dyeing in a picric acid bath. The picrate of lead formed is very explosive, either when heated or struck, and silk dyed in this way burns when ignited like guncotton. Consequently this process must be considered very dangerous.

Naphthol yellow, $C_{10}H_5(NO_2)_2ONa$, and naphthol yellow S., $C_{10}H_4(NO_2)_2ONa\ SO_3Na$, have also been used. They were applied like picric acid, but since the introduction of the azo dyes their use has declined.

DANGEROUS MATERIALS USED IN THE TEXTILE, DYEING AND OTHER INDUSTRIES.

The following is a short list of those substances which have caused fire or which appear likely to be dangerous, with a brief indication of the conditions which may serve to render them so.

(1) *The Oils.*—These have already been discussed.

(2) *Volatile solvents* find but limited use in textile industries and dyeing. A few are sometimes used in wool scouring, and methylated spirit is employed as a solvent for some coal-tar dyes. (For the properties of the volatile solvents see Chap. XI.)

(3) *Bleaching Powder.*—Although not of itself combustible, yet according to some authorities casks of

bleaching powder exposed to direct sunlight have been known to explode. It must also be remembered that not only is it a powerful oxidising agent, but also that in contact with acids bleaching powder evolves chlorine, which may cause the inflammation of certain oils, etc., as turpentine, although the authors have never heard of such a case occurring in works. If a cotton rag or other porous substance soaked in turpentine fell into a cask of bleaching powder it would probably burst into a blaze. There is a case on record where a fire was caused by bleaching powder coming in contact with methylated spirit.

(4) *Sodium and Barium Peroxide.*—According to Dr. Dupre, these substances when mixed with wood dust and struck cause an explosion, and even if the dry powder be placed on a deal board and rubbed with another board or struck, fire arises and spreads rapidly.* Consequently, when either of these substances is employed, care should be taken that the powder is not scattered about on the wooden floors, for the friction of the boots of a person treading thereon might cause fire.†

(5) *Strong acids,* such as sulphuric or nitric.

Under suitable conditions, although harmless of themselves, these substances may give rise to fire, and it would be well to point out some of these. (See also Chap. VII.) Turpentine is ignited by contact with *nitric acid.* As a strong acid it will liberate chlorine peroxide from chlorates, and so might cause an explosion if some of it accidentally fell on some potassium chlorate, especially if hot or mixed with some oxidisable substance. Cotton, too, might be ignited with strong nitric acid.

Sulphuric acid, although charring organic matter, such as cotton or sawdust, would hardly cause its ignition.

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* *Jl. Soc. Chem. Indus.*, 1897, p. 482.

† See also *Jl. Soc. Chem. Indus.*, 1894, p. 198.

With nitrates it liberates nitric acid and from chlorates, chlorine peroxide. Mixed with water, sulphuric acid causes a great increase in temperature. Water may be boiled by adding concentrated sulphuric acid to it.

Hydrochloric acid is much less dangerous, although it, too, will liberate nitric acid from nitrates and chlorine peroxide from chlorates.

(6) *Potassium and sodium chlorate* have already been described. (See Chap. VII.) It should be noted that of themselves these chlorates are generally harmless; only when mixed with other substances do they become dangerous.

(7) *Sulphur.*—The properties of this substance have already been sufficiently discussed.

(8) *Nitrates.*—Potassium and sodium nitrates and their use in the manufacture of explosives have already been described.

(9) *Lead Nitrate.*—When mixed with organic matter and subjected to rubbing or friction, lead nitrate may cause ignition.

(10) *Copper Sulphide.*—Freshly precipitated copper sulphide should not be kept in a moist and warm atmosphere, as it changes into copper sulphate by oxidation and evolves heat during the process.

CHAPTER XIV.

MISCELLANEOUS FIRE RISKS.

Dangers from Fire in Various Other Industries—Spontaneous Combustion.

In this chapter it is proposed to include a number of disconnected statements relating to fire and explosion risks in various industries and operations not described in the preceding chapters.

HEATING DUE TO OXIDATION BROUGHT ABOUT BY THE ACTION OF BACTERIA.

Many fermentative and putrefactive changes consist in oxidation (by the air) produced under the agency of the life processes of micro-organisms. Although the temperature resulting from the direct action of these organisms can never be dangerously high, yet in many instances the heat developed may, by increasing the rate of direct oxidation, eventually lead to an outbreak of fire. Examples of such production of heat are often met with; almost all heaps of decaying organic matter, *e.g.*, stable manure or tanners' refuse, show a high temperature in their interior. On a larger and more important scale, often resulting in actual combustion, hay which has been stacked when green or imperfectly dried offers a good example. The micro-organisms, which are always abundant in grass and hay, act upon the constituents of the woody fibre (mainly cellulose) and the sap, producing changes, attended with the absorption of oxygen and consequent heating.*

If the vegetable matter were freely exposed to the air, no harm would result from these changes, as the heat would be carried away as fast as evolved; or if the grass were strongly compressed, so as to squeeze out the air from its interstices (as, *e.g.*, in ensilage), the heat production would be checked. In most cases, however, neither of these methods is adopted, but the hay is stacked in huge masses, in a loose and bulky condition, containing, therefore, a large amount of air in the numerous interstices, and yet sufficiently tightly packed together to prevent its free renewal. The conditions are thus favourable to the life of the bacteria† (inasmuch as there is abundance of oxygen, and the escape of heat is prevented) and to the production of a high temperature. This latter favours the direct oxidation of the vegetable matter by air with a further exaltation of temperature, until under favourable conditions the actual point of ignition is attained, when rapid combustion (burning) sets in, and the stack may burst into flames. Generally, however, the heat being greater nearer the centre, where the access of air is difficult and slow, a smouldering combustion is produced.

The conditions favourable to the heating of haystacks are not exactly known, but it has been shown that a cer-

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* Frankland and Jordan (*Journal of the Chemical Society*, 1883, p. 294) examined the gases evolved during the conversion of grass into hay, and showed that they consisted mainly of carbon dioxide and, in some cases, of small quantities of nitrogen and hydrogen. They also found that the oxygen of the air surrounding the grass was quickly and completely absorbed, and that when the grass was kept under water large volumes of gas containing hydrogen as well as carbon dioxide were evolved, and that acetic, lactic and other acids were found.

† Only up to a certain point. Most bacteria are killed by temperatures oven below 100° C. (212° F.), although the spores of the hay bacillus can resist, for a short time, even a slightly higher temperature.

tain quantity of moisture is one of the most important. Obviously the danger is much greater in a large than in a small stack, and it can be decreased in various ways. The best method, and the one which first suggests itself, is to dry the hay very thoroughly, so as to prevent the growth of bacteria. This cannot always be done, nor is it an entirely satisfactory plan; for many purposes it is desirable that a certain amount of fermentation should take place, since by this means the aroma, flavour and colour of the hay are improved.

The two methods generally adopted if the hay has to be stacked somewhat green are:

(1) To mix salt with the hay as it is stacked. This probably acts by preventing or hindering the growth of the micro-organisms, while it renders the hay more palatable. Possibly it may act also as a fireproofing material or oxidation preventative for the fibres (?).

(2) The more efficient method is to ventilate the hay by several vertical air shafts, made at the time of stacking by including in the stack, sacks filled with hay, and drawing these up occasionally as the stack rises. Sometimes (often in Scotland) an open conical structure of wooden scantling is erected in the centre of the site chosen for the stack and the hay built around it. These methods depend for their success upon the removal of heat by circulation of air.

Other organic materials occasionally ignite from the heat produced by their fermentation when heaped in a moist condition. Thus, cases of the kind have been known with tobacco and with hops.

HEATING DUE TO MECHANICAL ABSORPTION OF OXYGEN FROM THE AIR BY POROUS SUBSTANCES.

Instances of this kind have already been mentioned, *e.g.*, recently burnt charcoal and certain kinds of coal are believed to suffer spontaneous combustion from this cause. (See chapter on fuel.)

It is a well-known fact that any condensation, even compression of a gas, develops heat. The gases absorbed by charcoal must be considerably condensed in its pores, and since it is a poor conductor of heat, a high temperature is easily attained, unless cooling by air circulation can take place. When the temperature rises to a certain point, oxidation begins and proceeds until the ignition point is attained, which in some specimens of charcoal is very low. (See Chap. V.) Powdered charcoal or coal, by presenting a greater surface, is more liable to produce this effect than the massive form.

HEATING DUE TO SLOW OXIDATION, COMMENCING AT THE ORDINARY TEMPERATURES.

This is a more fruitful source of fires than either of the above-mentioned causes.

The most notorious examples of this action are provided in—

(1) Certain oils when spread out on cotton, linen or wool;

(2) Iron pyrites in coal, and

(3) Phosphorus.

These cases have been dealt with at some length. (See Chaps. V. and X.)

In all cases the danger lies in the possibility of the heat generated by the slow oxidation raising the temperature to the point of ignition, when ordinary rapid combustion or burning commences.

One method, and a very effective one if it can be adopted, of preventing such a catastrophe is thorough ventilation, whereby the heat is conveyed away by the air and a dangerous rise of temperature prevented. Another point to be remembered in this connection is that the rapidity with which oxidation occurs increases rapidly with a rise of temperature. The proximity of any source of heat, *e.g.*, hot-water or steam pipes, therefore, greatly increases the risk. With reference to ventilation, it is found that partial ventilation is worse than none at all, and may actually increase the rate of oxidation. In the case of four ships carrying coal containing pyrites to India some years ago, three were provided with air shafts through the coal, and were lost, owing to spontaneous combustion, while the fourth, which had no provision for ventilating the hold, reached its destination safely.* The writer just quoted calls attention to the increased risk from this cause if the coal be loosely packed, so that by the rolling of the vessel its fragments may be moved about and crushed, so constantly exposing fresh surfaces for oxidation. He also recommends that coal stacks should never exceed 2.5 metres (about 8 feet) in height.

Heating Due to Chemical Changes Occurring in the Material or Materials Themselves.

Instances of this kind have already been mentioned and discussed, *e.g.*, in aniline black dyeing the heating of the fabric after ageing is due to chemical changes taking place between the constituents employed in the process—the aniline salt and the oxidising substance (generally chlorate)—and it is probable that only when the temperature of ignition is nearly reached, does the oxygen of the air begin to take an active part in the reaction.

Reactions of this kind are exceedingly numerous. In fact, as already explained, almost all chemical reactions are attended with the development of heat. A few of the

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* Quoted by L. Häpke, *Chemiker Zeitung*, 1893, 17, 916.

more commonly occurring or interesting reactions attended with a dangerous rise of temperature are the following:

(1) *The Slaking of Lime.*—Quicklime, CaO, when brought into contact with water, produces slaked lime, CaH_2O_2, and this change evolves a very large amount of heat. If the quicklime be very pure (so-called "fat" lime), the heat is evolved very rapidly, and so a high temperature, often 150° C. (302° F.), is attained. This temperature is sufficient to ignite some easily inflammable materials, *e.g.*, carbon disulphide, sulphur or phosphorus, and hence may give rise to danger, unless properly conducted.

(2) *The Dilution of Sulphuric Acid.*—This has already been discussed. (See Chap. VII., p. 122.)

(3) *The Action of Water on Calcium Carbide.* (See Chap. VI.)

(4) *The Interaction Between Water, Sulphur and Iron Filings.*—This reaction begins slowly, but gradually becomes more and more rapid, until, finally, a high temperature results and sparks are actually produced. A mixture of powdered sulphur and iron filings, buried in damp earth, constitutes the so-called "Lemery's" volcano, familiar to many schoolboys. Our reason for mentioning it here is that it has been suggested that some outbreaks of fire in engineers' workshops may have been due to a similar action taking place in the space between the floor of one room and the ceiling of the one below, owing to the accumulation of iron filings there and the damping of these by the water used in watering the floor. The suggestion does not appear very plausible, as it is difficult to see how the sulphur should come to be in such a position!

Heating by Electric Sparks.

Electricity is often generated by friction of non-conducting substances. To be non-conducting it is essential that substances be free from water; so it is found that electricity is only generated by the friction of *dry* substances. Metals being conductors, do not show any production of electricity, even when dry. When a body becomes electrified it tends to lose its electricity by sparking toward any other body in its neighbourhood, and as an electric spark has a very high temperature, it may easily ignite an inflammable substance. One instance of danger from this cause has already been pointed out—the grinding of sulphur (see Chap. VIII.); belting, wooden shoots in a malthouse, and many other articles may under suitable conditions develop electricity in this way.

It is also to be noted that while objects which are wetted with water are good conductors, and do not become electrified by friction, the same is not true when they are wetted with other liquids, *e.g.*, benzine. Cases have occurred where fire has arisen through the inflammable vapours given off by this liquid becoming ignited by electric sparks, produced by rubbing articles of clothing with flannel moistened with the benzine ("dry cleaning").

Reference may here be made to a paper in the *Leipziger Färber Zeitung*, 1899 (3), 105, on the dangers attending the use of petroleum spirit in "chemical" cleaning establishments. Attention is called to the fact, shown by Fischer and Richter, that aqueous vapour lessens the explosibility of a mixture of benzine vapour and air. As the vapours are heavier than air, ventilation by the usual plan of removing air from the upper portion of a room is of little service in freeing the atmosphere of these vapours.

The ventilation should be effected by suction through pipes opening on the level of the floor. No fires or naked flames should be allowed in rooms where benzine is used.

In Germany, the police regulations insist on the use of safety lamps or of lights let into the walls and protected by air-tight glass from the atmosphere within the rooms wherever benzine, turpentine, ether, alcohol or other volatile solvent is employed or stored.

The pockets of wearing apparel should also be carefully searched for matches, since these do not lose their power of ignition by friction, even when soaked in benzine.

Richter has shown that the heavy vapours may flow along the surface of the floors, down staircases, etc., and may thus become ignited by a flame at a considerable distance and act like a fuse to the main bulk of the liquid.

The store of benzine or petroleum spirit is best made by sinking a tank in the ground in the open air and covering it with a light roof. From the tank, the benzine is pumped into the various rooms.

The rooms where the cleaning operations are conducted should be built with very light walls and roof, so that little resistance is offered should any explosions occur. Sand and moist earth are good for extinguishing a fire in such works, water is almost useless. Ammonia has, in several instances, proved very effective. At a "chemical" cleaning establishment in France, a vessel containing 200 litres (44 gallons) of naphtha became ignited; a person present threw a large bottle of strong ammonia solution into the flames. Its effects were astonishing; the flames were instantly extinguished, though dense clouds of black smoke were emitted for a few seconds.

Explosions and inflammation of mixtures of "petroleum spirit" vapour and air have also occurred with fatal results in connection with ladies' hair washes. Public attention was directed in June, 1897, to this matter by the death, in London, of a lady from injuries received at the hairdresser's, from this cause. In this case no flame was near, and, according to Lord Kelvin, the probable source of ignition of the inflammable vapour was an electric spark generated by the friction of the hair.

EXPLOSIONS FROM IGNITION OF DUSTY ATMOSPHERES.

These have already been alluded to. (See Chap. IV.) Any combustible powder, if finely divided and suspended in air, is explosive by contact with a flame or other source of heat. Some of the more important cases of the occurrence of such dusty atmospheres are:

(1) *Coal-Mines.*—In deep mines, where the temperature is high and water not very abundant, the air is always dry, that is, although it contains as much or more actual weight of moisture than the upper, outside air, yet, because of its higher temperature, it is relatively much drier. Consequently, all the materials in the mines become dry, and if the coal be dusty, large quantities of extremely fine and dry coal and shale dust are found in all parts of the mine. Though there are very few if any authenticated cases in which a colliery explosion is to be attributed solely to dust, yet there is not the slightest doubt that explosions occur in such dusty mines of a violence incomparably greater than could possibly be accounted for by "firedamp." The presence of a quantity of firedamp, which could be ignored with safety in a damp mine, may give rise to a most disastrous explosion in a dusty one. Once an explosion starts, even if it be of a trifling and insignificant character in itself, in such a mine it stirs up a quantity of

the dry and inflammable coal dust; this then explodes, stirring up more dust, and thus the explosion propagates itself along galleries which may be quite free from fire-damp, and the destruction wrought is often enormous. Not only is the explosion itself very violent and devastating, but the "after-damp," *i.e.,* the mixture of gases left after the explosion, contains, almost invariably, large quantities of carbon monoxide, a deadly poison. Coal dust has played a very important part in almost all the great colliery explosions of recent years.

Many attempts to lessen the dangers in such mines have been made. Some were directed to the "slaking" of the dust either by frequent applications of water or by the occasional watering of the galleries and airways of the mine with solutions of deliquescent salts, like calcium chloride. These salts absorb water from the air, and retain it tenaciously; thus they are always damp, and fix the dust.

(2) *In Flour Milling, and in Screening and Dressing Malt and Grain.*—In these operations large quantities of very finely divided matters, composed mainly of starch, are produced. If these become disseminated through the air within the mills, ignition at an open flame or other source of heat is followed by an explosion. Such explosions are often extremely violent and destructive.* Heated bearings are also likely to occur in mills, and may be the cause of fire.

(3) *In Rag Grinding.*—The rapidly running machinery in this operation gives rise to a considerable amount of dust, especially if little oil be used, and if the rags contain cotton, the dust is highly inflammable. An even

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* For example, at Glasgow, in July, 1872, and at Minneapolis, in May, 1878. The latter was of almost inconceivable violence, sheets of iron roofing, 6 ft. x 2 ft., being projected more than two miles, and a column of flame and smoke, estimated at 600 ft. in height, being produced.

greater danger is in shaking out the cotton from wool after "carbonising" union rags in the preparation of "extract" wool. (See Chap. XIII.) Naked flames and sparks, struck by friction, from hard fragments (buttons, etc.) in the rags, are likely causes for initiating explosions or inflammations of the dust thus produced.

(4) *In the Grinding of any Inflammable Materials.*—Many hard substances, when ground either in mills or mortars, or in Carter's disintegrator, yield large quantities of dust, and thus present risk of explosion and fire. Myrobalans, used by tanners and dyers, are such hard substances, and in a recently published tariff for tanneries of the Fire Offices' Committee an extra charge is made if these are ground on the premises.

Another operation attended with the same dangers is snuff grinding. Dust explosions have also occurred in connection with oatmeal, starch, rice, malt, sawdust, zinc, and even dry soap.

All materials may be classed in the following groups, according to their behaviour toward fire:

(A) INCOMBUSTIBLE BODIES.—These include substances like stone, brickwork, iron and other metals.

(B) BODIES WHICH ARE COMBUSTIBLE OF THEMSELVES, WITHOUT ACCESS OF AIR.—These include all explosives, both compounds like nitroglycerine, etc., and mixtures like gunpowder, various fireworks, etc. To this class belong also celluloid and similar bodies containing collodion (*i.e.*, nitrated cellulose) and camphor. Certain gases, *e.g.*, chlorine peroxide and many mixtures of inflammable gases with air or oxygen, belong to this class.

(C) COMBUSTIBLE SUBSTANCES, *i.e.*, bodies which oxidise in air under suitable conditions with the evolution of much heat. This is a very important class, and may be divided into three groups:

(i) *Gases.*—These have already been fully discussed.

(ii) *Liquids.*—These may conveniently be divided into—

(a) With flash-points below the ordinary temperatures. These liquids are especially dangerous, on account of their evolving vapours, which may travel and ignite at a flame or fire some distance away, and thus carry fire to the vessel containing them.* Such liquids are the volatile "petroleum spirits," cymogene, rhigolene, etc. (see petroleum, Chap. IX.), naphtha and benzol from coal-tar, ether, alcohol, turpentine, acetone, amyl acetate, carbon disulphide, etc. (see Chap. XI.), or preparations containing these substances.

Preparations containing volatile solvents, particularly the various petroleum "spirits," are very numerous and have frequently given rise to fires and explosions. In September, 1888, a petroleum-laden boat, "United," exploded at Bristol, killing three men and shattering all the windows within a hundred yards of the spot. In Col. Majendie's report on the accident it is stated that the cargo consisted of deodorised naphtha in 42-gallon casks, many of which were leaky, that one volume of petroleum spirit yields 141 volumes of vapour, which renders any volume of air between 3000 and 16,000 inflammable.

In 1880 and 1881 several serious explosions, attended with considerable loss of life, occurred on board various steamers and warships, amongst others on H. M. S. "Cockatrice," "Triumph" and "Doterel." † These were traced in nearly all cases to a "drier" (for use with paints) which contained petroleum spirit. So, too, acci-

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* Cases have been known where ignition has occurred at a flame 60 feet from the point of leakage.

† See *The Engineer*, vol. 53 (1882), p. 49; also vol. 51 (1881), pp. 411 and 413.

dents have happened through the ignition of the vapours of petroleum spirit (flash-point 45° F.) used in the preparation of the paint for the interior of water-ballast tanks on steamers (*e.g.*, in April, 1896, on the Cunard S.S. "Servia").

A remarkable explosion occurred at Rochester, N. Y., in December, 1887, owing to the escape of naphtha (flash-point 13° F.) from a dislocated three-inch pipe into a neighbouring sewer and the ignition of the vapour at a distant boiler fire. The explosion killed three, and injured twenty men, destroyed much property and inflicted a loss estimated at £50,000.

It has been stated that the volatile petroleum products, benzoline, etc., may be rendered safer for use in lamps by adding alum, ammonium chloride or camphor to them, but, according to some experiments described in a paper read in December, 1898, before the American Chemical Society by its president, Prof. C. E. Munroe, from which the above cases are quoted, these substances are useless for the purpose. Alum and ammonium chloride are practically insoluble, and produce no effect upon the oil, while camphor, which is readily soluble, raises the flashing point, but lowers the temperature of ignition.

(b) Liquids flashing at a temperature slightly higher than the ordinary one. These, though not emitting inflammable or explosive vapours, and, therefore, not capable of being ignited by a lighted match at the ordinary temperature, become possessed of the same properties as class (a) when slightly warmed. Petroleum or kerosene is the best example of this class.

(c) Liquids with high flash-points. These are not inflammable, except at a high temperature, and will burn only from a wick, or when made hot. They include the animal and vegetable fatty oils and the heavy lubricating mineral oils. They present little risk, but, of course, increase the fierceness of a conflagration if stored in large quantities, when an outbreak of fire occurs.

(iii) *Solids.*

(a) Fusible solids, yielding inflammable vapours when heated to a higher temperature. In this class are fats, waxes, resins, fatty acids, some solid hydrocarbons, *e.g.*, naphthalene or "albo-carbon," from coal-tar, paraffin, sulphur and phosphorus. When melted they are similar in properties to the liquids of class (c). Their properties have already been described.

(b) Solids which do not fuse, but which evolve inflammable gases by destructive distillation. They are very numerous, and include most organic substances, like wood, coal, etc. Many of them have been described in the chapter on fuel.

(c) Solids which are not volatile. These are rare, the best representatives of the class being coke and charcoal. These have been described. (See Chap. V.)

(D) OXIDISING SUBSTANCES, *e.g.*, nitrates, chlorates,* etc. These substances and their functions in aiding combustion have already been described. (See Chap. VII.)

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* Potassium chlorate was undoubtedly the main factor in a disastrous explosion which occurred at St. Helen's in May, 1899, as an after effect of a fire at Kurtz's chemical works, where over 150 tons of the chlorate were stored in a pure state.

The result of the official inquiry has, we believe, not yet (September, 1899) been made public; in all probability the explosion, which was excessively violent (it was heard 27 miles off), was due to either—

(1) The liberation of chlorine peroxide, a strongly endothermic gas, and, therefore, very explosive, by the action of the oil of vitriol, which was stored in large quantities close at hand, upon the chlorate, or

(2) The effect of heat upon the chlorate itself. Potassium chlorate is endothermic, and if the temperature of a large quantity of it were suddenly raised, the oxygen might be evolved explosively and the whole might then detonate. (See paper by C. A. Lobry de Bruyn, abstracted in *Jl. Soc. Chem. Indus.*, 1899, p. 786.)

CHAPTER XV.

FIRE PREVENTION AND EXTINCTION.

Fireproofing of Textile Fabrics, Paper and Wood—Methods Used for Extinguishing Fire—Sprinklers—Extincteurs.

All materials, excepting metals, brickwork and stone, are susceptible to the action of fire; indeed, if the temperature be high enough even these substances are melted or disintegrated. Such excessively high temperatures, however, are of comparatively rare occurrence, and consequently it is usual to term a building constructed entirely of brick, stone and iron—fireproof.

It does not come within the scope of this work to describe the methods employed in the erection of such structures, this belonging rather to the province of the architect than that of the chemist.

In this chapter the methods adopted for rendering certain inflammable materials more or less "fireproof" will be briefly considered.

The chief materials requiring notice are textile fabrics in general, especially cotton and linen goods and woodwork of all kinds.

Vegetable fibres are far more inflammable than those of animal origin. Their main constituent is *cellulose,* so that, chemically speaking, cotton, linen, jute, etc., are almost identical with wood.

When vegetable matter is gradually heated it undergoes a series of changes. (See charcoal, Chap. V.) At a temperature of about 200° C. (392° F.) it becomes light brown in colour and loses considerably in rigidity; at 300° C. (572° F.) it is charred, though without flame, and is practically destroyed. Direct contact with flame, however, if air be present, causes it to take fire at once and to burn away completely.

Both vegetable matter and charcoal are bad conductors of heat, and if they could be prevented from being converted into gaseous products they would protect the interior from the heat around them. It is impossible to prevent the heat converting the wood on the exterior into vapours, gases and charcoal, nor can these vapours and gases be prevented from burning when they come in contact with air, but it is possible to hinder, if not to entirely stop, the oxidation of the charcoal; obviously any device that will exclude oxygen will do this. The wood then becomes encased by a layer of bad conducting charcoal, is protected from further oxidation or injury and is practically uninflammable.

The best method of attaining this exclusion of air or oxygen is therefore the important thing to search for.

Two principal ways suggest themselves—

(1) To coat the material with an impervious, uninflammable varnish.

(2) To surround the wood with a constantly renewed atmosphere of indifferent gas or vapour.

Substances which have been subjected to fireproofing treatment consequently carbonise under heat, but do not inflame or afford any aid to the spreading of the fire; moreover, they are easily extinguished. The surfaces of such substances can withstand even an intensely high temperature for a short time, but if they are exposed to the long-continued action of heat they undergo destructive distillation (exactly as in the manufacture of charcoal), and their strength is destroyed just as if they had not been rendered "fireproof."

Fireproofing then, simply, means that the substance is treated in such a way as to prevent its inflaming under conditions which would be quite capable of producing immediate inflammation of the substance in its usual state. Absolute fireproofing is impossible.

FIREPROOFING OF TEXTILES.—These are only treated in the piece form.

The materials are always applied in solution, and the solvent, usually water, is expelled by drying. Two distinct classes of substances are employed—

(1) Soluble substances. These are applied in one operation, either by spraying the solution on the cloth as it passes in open width into the drying chamber or, better, the fabric is simply padded with the solution and dried.

(2) Insoluble substances. These are formed in the fibre by applying one solution to it, drying and then applying the second solution, when chemical action, resulting in the separation of an insoluble substance on the fibre, takes place.

The first class of bodies are not useful for goods which have to be washed, but on account of their easy application are generally employed for dress goods, curtains, etc.

It is of the utmost importance that the fireproofing material be thoroughly disseminated throughout the whole mass of the fibre.

The chief desiderata of a good fireproofing material are that it—

(1) Possesses in a large degree one or more of the following properties:

(a) The power of forming, when heated, gases or vapours which are not inflammable and non-oxidising, so as to yield an atmosphere incapable of aiding the combustion of the fabric itself.

(b) The power of yielding, when heated, a readily fusible, continuous layer of residue which coats the partially charred fabric and excludes oxygen from it.

(2) That it does not confer undue stiffness or harshness to the fabric, nor readily fall off in the form of powder or scale, when the cloth is crumpled or bent.

(3) That it does not affect the strength of the fabric itself, nor have any action upon the colours with which it may be dyed.

(4) That it is not deliquescent (*i.e.,* absorbs moisture from the air).

(5) That it is not poisonous, odorous nor expensive.

SOLUBLE SALTS.—As already stated, these substances cannot advantageously be applied to fabrics which have to be washed, since washing would completely remove them from the fibres. They are, as already said, in very general use on account of ease of application. Many different substances and mixtures have been employed. The most important ones are sodium tungstate and ammonium phosphate. Among many others the following may be mentioned:

Alum, $Al_2(SO_4)_3K_2SO_4.24\,H_2O$, and *aluminium sulphate,* $Al_2(SO_4)_3.18H_2O$.—These substances confer a certain resistance to fire, but are objectionable on account of their rendering the fabric brittle and their liability to injure the colours of many dyed cloths.

Ammonium Sulphate, $(NH_4)_2SO_4$, and *phosphate,* $(NH_4)_3PO_4$.—These are excellent and are suitable for all goods which do not require ironing. They owe their efficacy to the fact that when strongly heated they evolve ammonia, steam and, in some cases, nitrogen; these gases protect the material from air. In the case of the phosphate, metaphosphoric acid, HPO_3, is probably left and acts as a fusible, non-porous coating to the charred organic matter; this coating acts beneficially in excluding air and also in hindering, by its bad conductivity, the access of heat to the organic matter beneath.

Borax, $Na_2B_4O_7 . 10\,H_2O$.—This salt serves as an excellent protector. It probably acts in two ways; at first, by the evolution of its water of crystallisation, which absorbs heat and drives away the air from contact with the inflammable substance, then afterwards, the anhydrous salt fuses and forms an oxygen excluding varnish.

Calcium Chloride, $CaCl_2$.—This substance is deliquescent, *i.e.,* it absorbs moisture from the air in sufficient quantity to dissolve the salt. It has been recommended by Sir F. Abel for rendering rope mantelets, used on warships, uninflammable. This it does mainly by keeping them damp.

Ammonium Calcium Sulphate, $CaSO_4(NH_4)_2SO_4$.—Gypsum or calcium sulphate is almost insoluble in water; it is much more soluble in ammonium sulphate solution. Fabrics treated with such a solution are rendered very fire-resistant. This substance was strongly recommended by Patera, an Austrian chemist, who claimed that it was in some respects superior to sodium tungstate.

Magnesium borate really belongs to the insoluble salts, but, as it forms only slowly when solutions of borax (sodium borate) and magnesium sulphate, $MgSO_4$, are mixed, it can be applied in one solution. Its use was introduced by Patera, who recommends that the fabric be immersed in a solution containing 3 parts of borax, 2.5 parts of magnesium sulphate (Epsom salts, $MgSO_4 . 7\,H_2O$) in 20 parts of water and the necessary amount of starch, then wrung between cloths and dried.

The fabric thus becomes coated with insoluble magnesium borate, which is as resistant to fire as sodium tungstate, is not removed by washing, does not injure the most delicate colours and is very cheap. The solution must be prepared very shortly before use, otherwise the insoluble borate might separate out. The addition of a little ammonium chloride is recommended.

Sodium silicate, "water glass," Na_2SiO_3, confers non-inflammability, but renders the fabric stiff and in many cases affects the dye.

Sodium tungstate, $Na_2W_4O_{13}.10\ H_2O$, is excellent for the purpose and has found extended applications for curtains, ladies' dresses, etc., as it does not affect the colours of dyed fabrics. It is improved by the addition of a small quantity of sodium phosphate, $Na_2HPO_4.12\ H_2O$.

INSOLUBLE SALTS.—These are precipitated on the fibre by the plan already mentioned, viz., first impregnating with a saline solution, drying, and then treating with a second solution, which, by interaction with the substance present in the first, will form an insoluble compound. They possess the advantage over the soluble salts that they are not removed from the fabric by washing. Substances which have been so used are numerous, including the borates, phosphates and silicates of barium, calcium, strontium, magnesium, zinc, iron, aluminium, copper and lead.

Alumina, $Al(OH)_3$, precipitated from sodium aluminate and sodium bicarbonate, has been found to be an excellent material for the purpose, a very small quantity sufficing.

Gelatine, precipitated on the fibre by first treating with aluminium acetate ("red liquor" of the dyer) and then with gelatine solution, has also been used.

FIREPROOF PAPER.—For rendering paper non-inflammable similar methods are used, the solution being applied at the conclusion of the manufacture of the paper, but before the drying.

Totally incombustible paper is also prepared in several different ways, but in all the basis used is asbestos. Generally the asbestos pulp is mixed with a small quantity of wood pulp or ordinary paper pulp and with borax and glue. Sometimes water glass is also added. A fireproof ink for writing consists of an ammoniacal solution of silver nitrate and India ink.

For printers' use the addition of platinum chloride to lampblack and varnish yields an indestructible ink.

FIREPROOFING OF WOOD.—Woodwork can be rendered more or less fireproof with the same materials as are used in the case of textile fabrics.

Two methods of application, however, can be employed—

(1) By applying to the exterior of the wood a solution of the materials or a coating of fireproof paint.

(2) By impregnating the whole body of the wood with the fireproofing material.

Many substances have been proposed and used for the purpose—alum, water glass, copper sulphate, borax and magnesium sulphate, ammonium sulphate, ammonium phosphate, zinc chloride, etc.

Impregnation of the wood with the fireproofing material is carried out by a process similar to that used for impregnating timber, *e.g.*, railway sleepers with preservative solutions like creasote, etc. The wood is placed in a closed vessel, the air removed, and a solution of the fireproofing substance admitted; this slowly penetrates into all parts of the wood. Sometimes the solution is boiled in contact with the timber.

The substances found most useful for the purpose are magnesium borate, sodium tungstate and, especially, ammonium phosphate.

For external application sodium silicate is the most efficacious, especially in conjunction with asbestos and sodium aluminate.

Fireproof coatings generally consist of two kinds of ingredients, the vehicle and pigments, though a certain amount of resistance to fire is imparted by merely coating the wood with a solution of certain substances, like sodium tungstate or silicate.

As *vehicles* the following are used—

(1) Sodium silicate solution, "water glass"; this is the best of all, as it is itself non-inflammable.

(2) Sodium aluminate solution ($Na_2Al_2O_4$) is also excellent, and is often used in conjunction with the above.

(3) Size, glue or starch paste. These are combustible, but not readily inflammable; when exposed to fire they burn and leave the pigment as a protective coating.

(4) Linseed oil, though very inflammable when fresh, becomes much less so when oxidised by exposure to air.

As *pigments* many substances are employed, among the most suitable being asbestos powder, oxide of iron, slag meal, Portland cement, lime and whiting. The most effective protector is *asbestos paint,* consisting of water glass (sodium silicate), sodium aluminate and asbestos, especially if three coats be given. Several varieties of asbestos paint are on the market.

Other rough methods are sometimes used with success, *e.g.,* the applications of a coating of sodium silicate, then one of lime and finally a second coat of silicate.

As showing the increasing attention being paid to fire-resisting materials we may mention the opening of a Testing Station (January, 1899) by the recently formed (1897) British Fire Prevention Committee, where various "fireproof" materials are to be systematically tested and reported upon. This station, the first of its kind in England, was erected under the supervision of Mr. E. O. Sachs and a sub-committee.* Several institutions of this character have existed for some years in America, *e.g.*, in Denver, and on the continent, *e.g.*, Berlin.

FIRE EXTINCTION.—When a fire has started it can be extinguished by one of two methods—

(1) By cooling the combustible materials and the air at their point of contact, *i.e.*, the flame, to a temperature below the ignition point.

(2) By excluding air from the burning mass, thus stopping the chemical change, oxidation, which produces heat.

In practice a combination of the two methods is usually employed.

The first is generally carried out by throwing water on the burning material. Water is the best substance for cooling purposes, on account of its enormously high specific and latent heats. (See Chap. III.) A given weight of water, therefore, possesses greater cooling power than the same weight of any other substance at the same temperature.

A description of the appliances used for discharging water at a conflagration belongs to the province of the engineer rather than to that of the chemist, and will not be given here. Reference, however, may be made to the application of water by means of automatic sprinklers.

SPRINKLERS.—Automatic apparatus for the extinction of fires was invented many years ago. Thus, in 1763 a patent was granted to a Mr. Green for such an appliance. Again, in 1806 an automatic sprinkler was patented by John Carey, whose arrangement consisted of perforated pipes connected with a tank and closed by valves operated

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* See *Engineering*, February, 1899.

by weighted levers and kept closed by means of strings. By the burning of these latter the water was admitted to the pipes and distributed over the building. Many other devices were subsequently patented, but none seems to have been put into practice. In 1864 an arrangement was designed by Harrison in which a rose was kept closed by a valve held in position by a rod soldered by fusible metal. This apparatus was not generally adopted, and it was not until 1875, when Parmalee, in New Haven, Connecticut, invented his sprinkler, that the use of various forms of these appliances began to be general, at first in America, and some years later in England.

Almost all automatic sprinklers depend upon the use of alloys melting at a low temperature, generally about 69° C. (156° F.), but sprinklers intended for special purposes, *e.g.*, for use in drying stoves, are provided with fusible solder of suitable melting point (often 200° F. or higher). The fusion of the alloy releases a valve, through which the water flows, and is scattered by suitable means over a considerable area beneath the sprinkler.

Fusible alloys can be prepared of very different melting points.

The composition of several of the better known is given in the following table:

	Newton's.	Darcet's.	Rose's.	Wood's.	Lipowitz's.
Tin	3	1	7	2	4
Lead	5	1	8	2	8
Bismuth	8	2	14	7- 8	15
Cadmium	..	..	..	1- 2	3
Melting point...	94.5°	93°	80- 90°	66- 71°	60° C.
" " ...	202°	199.4°	176-194°	150-160°	140° F.

It is remarkable that the above melting points are all considerably lower than even the lowest of those of the constituent metals—

Tin	melts at	.........227° C.	or	440° F.
Lead	"	.........325° C.	"	617° F.
Bismuth	"	.........268° C.	"	514° F.
Cadmium	"	.........320° C.	"	608° F.

The most important points about a fusible alloy for use in sprinklers are—

(1) That it possesses a distinctly marked melting point, and does not soften much before it becomes actually fluid.

(2) That it does not undergo change by mere lapse of time. Some alloys disintegrate even under ordinary conditions, and more readily if subjected to alternations of temperature, owing to their constituents tending to separate and undergo partial crystallisation; this often raises the melting point.

(3) That it is not corroded by contact with air. In many cases, owing to the presence of acid vapours, etc., corrosion of almost all metals exposed to the atmosphere becomes inevitable; a coating of varnish is therefore often used to protect the fusible and other metal fittings of the sprinkler.

There are many forms of automatic sprinklers in use, but they may all be referred to one or other of two classes; indeed, they nearly all belong to the second class—

(1) *"Sealed" or "water-joint" sprinklers,* in which the outlet is closed by a plug or cap held in position by fusible solder. The water in such sprinklers comes into direct contact with the fusible metal, except in "dry-pipe" installations.

(2) *"Valve" sprinklers,* where the valve which closes the outlet is held in position by means of levers, struts or yokes, soldered together or to some fixed part of the sprinkler head by the fusible alloy.

The "sealed" sprinklers possess certain advantages in strength and freedom from danger of leaking, but as the fusible metal is in close contact with water or with the large metallic mass of the head, they are less sensitive and do not open as quickly as is desirable on the outbreak of a fire. Indeed, in England the use of sealed sprinklers has entirely ceased.

In the construction of the second form of sprinkler much ingenuity has been exercised, and a large number of different forms are offered for sale; of these about a dozen have been officially recognised by the Tariff Office Committee, although only about three or four patterns are in general use. A brief description of these may be of service—

(1) *The "Grinnell,"* introduced in 1882, was the first "valve" sprinkler commercially successful, and, in its improved form, is still the most popular.

Originally the essential features of this sprinkler were the use of a flexible diaphragm D as a valve seat and the ingenious way in which the valve E was held in position by an arrangement of struts and levers C and B. (Fig. 42.)

The valve was free from any danger of leakage, as the water pressure kept the flexible seating tightly pressed against the metal valve. The latter, when released by the melting of the solder at A, fell a short distance, and was then held by the outer framework, and served as a deflector. This sprinkler was very successful and found an extensive sale.

The main objections in practice were the effects of corrosion exerted by the water upon the valve itself, and by the air or any acid vapours present upon the metal struts and levers; this corrosion was liable to interfere with the opening of the sprinkler.

In 1890 an improved form was devised by Mr. Grinnell, and this has supplanted the older one. The risk of corrosion was overcome by making the flexible valve seat (A) of German silver and the valve itself of a glass hemisphere (B), held in position by an ingenious arrangement of levers (C, D and E), shown in Fig. 43. The levers are also of German silver, and all the portions in contact with each other are soldered with fusible metal, so that when the latter fuses the motion of the levers themselves is rendered easy, even if they be externally corroded, by the lubrication which the molten solder affords. When the alloy melts, B, C, D and E fall away and the water issues through A and strikes the deflector F.

Another advantage claimed for the Grinnell over all other forms of sprinkler is that, not only does the flexible valve seat insure freedom from leakage, but by its giving way slightly, and so following the glass valve, it keeps the water back until the solder has completely melted and the valve is quite free to open. This prevents an accident to which many sprinklers are liable, viz., in case of outbreak of fire the solder sometimes first softens and allows the valve

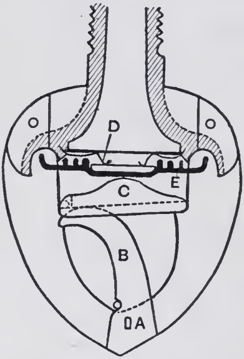

FIG. 42.—Grinnell Sprinkler, original form.

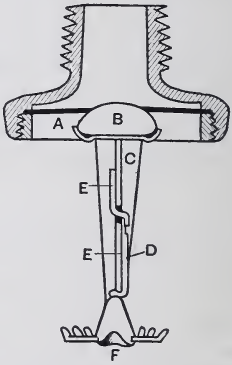

FIG. 43.—Grinnell Sprinkler, improved form.

to open slightly, thereby permitting the water to flow on to the soldered portion before it is entirely freed; further opening of the valve is thus prevented and the sprinkler becomes practically useless.

Of the many other forms of sprinklers which have been devised, only two or three are in extensive use. These include the following—

(2) *The "Witter."*—The construction of this will be understood from Fig. 44. It will be seen that the final adjustment of the pressure of the valve upon its seat is attained by means of a screw, which, however, does not pass through the bottom lever, as in some forms of screw-adjusting sprinkler, but through an upper cam or lever so arranged that the pressure on the fusible joint (which is just below the deflector) is only a small fraction of that exerted by the screw upon the valve. This plan lessens the risks of giving way of the solder and consequent leakage. The original form of the "Witter" gave an upward distribution to the water, which was claimed as an advantage, but in a later form this has been abandoned

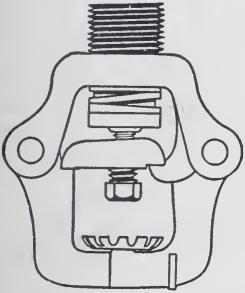

FIG. 44.—Witter Sprinkler.

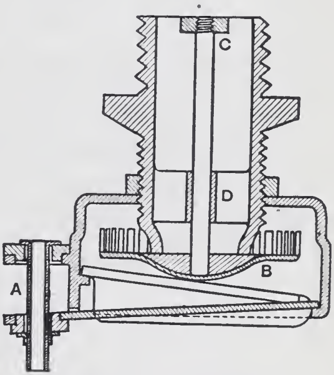

FIG. 45.—Titan Sprinkler.

and the more generally used plan of downward distribution adopted.

(3) *The "Titan."*—The details of this sprinkler are shown in Fig. 45. It will be seen to resemble the "Witter" in the arrangement of its levers, but differs in the deflector and the way in which the fusible joint is made. The latter consists of a hollow cylinder A with two rings upon it, passing through two holes, one in the bottom lever, the other in a lug cast on the side of the sprinkler head. The fusible metal is cut off from metallic contact with the body of the sprinkler by means of small boxwood collars. This is intended to prevent conduction of heat from the joint, and thus to render the apparatus more sensitive to changes of temperature. The deflector B acts as the valve and when released by the fall of the levers falls until C rests upon the fixed collar D.

In all sprinkler installations an adequate water supply is an absolute essential. The rules of the Fire Offices' Committee enact that two sources of supply must be available; these may be—

(1) Town's water.
(2) Elevated tank or private reservoir.
(3) Pressure tank.
(4) Pumps.

The use of sea water is forbidden, doubtless because of its corrosive action upon the pipes and sprinklers. Town's water must give a pressure of at least 10 pounds on the square inch in the highest sprinkler. A private tank or reservoir must have a capacity of at least 5000 gallons if not more than 150 sprinklers are used, and must be larger if there are more than this number. Its base must be at least 15 feet above the level of the highest sprinkler.

Another very important matter in connection with an installation is the automatic alarm, which should announce the opening of a sprinkler or the leakage of a pipe or joint as promptly as possible.

Various devices are employed, one of the most widely used being based upon the opening of a valve immediately the pressure on one side is released by an escape of water. This large valve is double seated, so that when it rises water is admitted from the main to another pipe connected with a water motor, which is thus set in action. The motor is provided with revolving hammers, which strike, when in motion, a large gong, and so produce a loud noise, which is kept up as long as the water is escaping from the sprinkler system.

In cold climates, or even in England in buildings not efficiently heated, considerable trouble is caused by the water in the pipes and sprinklers freezing and, by the expansion consequent upon this, bursting the pipes, or in other ways rendering the system inoperative. This can be overcome by *"dry-pipe" installations.* In these the pipes and sprinklers are filled with compressed air, which keeps back the water. In some installations by the use of a differential valve, so constructed that the area offered to the water pressure is only a small fraction of that exposed to the compressed air in the pipes, it becomes possible for a pressure of air of, say, 10 or 15 pounds per square inch, to keep back the water when the latter is at a pressure of 80 or 100 pounds. The system of pipes is in such cases connected with an air-pump which has to be put into action periodically in order to make good the leakage, much more likely to occur with air than with water. In these installations the sprinkler heads are always placed above the pipes so that the water will drain from them.

A dry-pipe installation does not act so promptly in case of fire as an ordinary one, since when a sprinkler opens the air has to escape from the pipes before any water comes. Partly for this reason and partly because of the greater trouble and attention which they require, dry pipes are never used when the ordinary plan can safely be adopted. It is therefore usual, even in cold climates or in unwarmed buildings, to employ the dry-pipe method only in the winter and to return to the full-pipe system during the rest of the year.

Water acts, as already stated, when thrown upon burning materials, chiefly in two ways:

(1) By cooling the heated mass. This is effected partly by absorption of heat by the water in having its temperature raised to the boiling point (specific heat), but more by the absorption of heat consequent upon liquid water becoming gaseous water (latent heat).

(2) By surrounding the burning materials with steam, instead of air. This brings about extinction by stopping oxidation; for, although steam does oxidise carbon, of which most burning materials are largely composed, the process is an endothermic one, *i.e.*, it absorbs heat (see Water Gas), and, therefore, the production of carbon monoxide and hydrogen from steam and heated carbonaceous matter can only proceed for a short time, and with the effect of rapidly lowering the temperature of the heated mass. The "water gas" so formed may, in some cases, where water is sent on to a mass of intensely hot carbon, do harm in carrying fire to a distance, but in the majority of instances the harmful effect is negligible compared to the usefulness.

A steam pipe in a room or other closed space is an efficient and convenient means of subduing an outbreak of fire. This method is sometimes resorted to in oil boiling and in shoddy mills, in the rag-grinding machines. Fires may in the latter case break out, owing to heat produced by friction, and such fires are at once quenched in the machine by the use of a steam pipe with which they are fitted.

Other Fire Quenchers.—As has already been said, no other substance is capable of acting as efficiently as water, so far as cooling is concerned, but there are many substances which can act in the same way as, or even more efficiently than, water in excluding air. Thus the following materials are used for the purpose:

(1) *Sand.*—This is excellent, being perfectly efficient if it can be applied in quantity enough to entirely surround the burning mass. It is only employed in comparatively few places, *e.g.*, in chemical laboratories, match factories, varnish works, etc., but might with advantage be much more extensively used.

(2) *Textile Fabrics.*—Best of wool or silk. These, too, are very effective in the early stages of a fire, and are often used in checking domestic outbreaks, due to accidents with lamps, burning clothing, etc. Like sand, they act mechanically by shutting off contact between the burning substance and air by the interposition of a comparatively uninflammable layer of solid matter.

(3) *Saline Solutions.*—These are supposed to act partly by giving off incombustible gases, partly by encrusting the burning articles with a non-conducting or air-proof coating. They were largely used in various forms of *hand grenades* some few years ago, but in practice they are found of little service. The liquids used in these grenades varied very much in composition, often consisting of dilute solutions of chlorides of calcium, magnesium, sodium or ammonium, or sometimes of carbonate of soda. In all cases, the cost of the salts in solu-

tion formed a very small percentage of the selling price of the grenade.

(4) *Indifferent Gases.*—These act by excluding oxygen altogether from the flame or, more generally, by so diluting the oxygen that the heat produced by its union with the combustible is not generated fast enough to keep the temperature of the mass above that of ignition; hence, combustion stops.

In the choice of the indifferent gas to be used the main point to notice is that it be a heavy gas and, therefore, capable of only slow diffusion. On account of its high density, 2.2 (air = 1), *sulphur dioxide* would thus be eminently suited for the purpose, and it is sometimes so used. It is made by burning sulphur or, better, carbon disulphide in air (in the latter case, carbon dioxide is also formed). Cylinders of liquid sulphur dioxide have also been employed for the purpose of extinguishing fires. The great objection to its use is the irritating smell and poisonous action upon persons breathing an atmosphere containing even a small proportion of the gas.

Carbon dioxide is much more largely used, and has the advantage of not being poisonous, except when present in large quantities. The gas is very easily prepared by the action of any acid upon a carbonate. Calcium carbonate (marble, limestone or chalk) is the chief raw material used, but for fire extinctive purposes sodium bicarbonate is generally employed. The gas is colourless, incombustible and a non-supporter of combustion of all ordinary materials. It is soluble in water, one volume of water dissolving one volume of the gas. By increasing the pressure, the amount of gas absorbed is proportionately increased. Thus, in the manufacture of aerated waters, the gas is forced into vessels containing water, when it dissolves to an extent which depends upon the pressure. The liquid is then bottled, the gas remaining dissolved until the pressure is released by the opening of the bottle, when the excess of gas escapes and gives rise to the effervescence characteristic of these beverages. It is formed by the fermentation of sugar, and is, therefore, evolved in large quantities from breweries, etc. By high pressure it can be liquefied.

When present in air carbon dioxide greatly interferes with the burning of flames, and if its amount be large enough, it extinguishes them instantly. The proportion of carbon dioxide to air required to do this varies with circumstances. It depends mainly upon

(1) The combustible used, being much greater in gas-fed than in wick-fed flames;

(2) The temperature;

(3) Whether the oxygen of the air has been diminished or not by burning or respiration.

The following table shows some results obtained by Clowes and Feilmann* showing the influence of carbon dioxide and nitrogen upon flames:

		Extinctive mixture of carbon dioxide and air.			Extinctive mixture of nitrogen and air.	
Combustible	CO_2 added	O	CO_2+N	N added	O	N
Alcohol	14	18.1	81.9	21	16.6	83.4
Paraffin	15	17.9	82.1	23	16.2	83.8
Colza and paraffin.	16	17.6	82.4	22	16.4	83.6
Candle	14	18.1	81.9	22	16.4	83.6
Hydrogen	58	8.8	91.2	70	6.3	93.7
Carbon monoxide..	24	16.0	84.0	28	15.1	84.9
Methane	10	18.9	81.1	17	17.4	82.6
Coal-gas	33	14.1	85.9	46	11.3	88.7

If the combustible were allowed to burn in a confined volume of air, the composition of the extinctive atmos-

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* *Jl. Soc. Chem. Indus.*, 1894, p. 1156.

phere was different, owing to the oxygen having been consumed, as well as the carbon dioxide increased. The following table shows the results of some experiments on the subject, also by Clowes and Feilmann.*

Combustible.	Percentage comp. of residual atmospheres from the flames. Oxygen.	Nitrogen.	Carbon dioxide.
Alcohol	14.9	80.8	4.3
Paraffin	16.6	80.4	3.0
Colza and paraffin	16.4	80.5	3.1
Candle	15.7	81.1	3.2
Hydrogen	3.5	94.5	0
Carbon monoxide	13.4	74.4	12.2
Methane	15.6	82.1	2.3
Coal-gas	11.4	83.7	4.9

It is evident from the above numbers that it is impossible to give any particular proportion of carbon dioxide to air which will extinguish a fire, so much depends upon the character of the burning material, the temperature and other circumstances.

In practice it is generally found best to employ water charged with carbon dioxide. This can be directed by means of hose-pipes, etc., with greater certainty and to a greater distance than would be possible with the gas.

The so-called *"Extincteurs,"* so largely employed in buildings, are metal vessels containing a solution of sodium bicarbonate and a sealed glass vessel of strong sulphuric acid. The glass vessel is so arranged that it can be broken by a blow upon a small projecting knob, when the acid, coming into contact with the bicarbonate, liberates carbon dioxide—

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Sodium bicarbonate.}}{2\,NaHCO_3} = \underset{\text{Water.}}{2\,H_2O} + \underset{\text{Carbon dioxide.}}{2\,CO_2} + \underset{\text{Sodium sulphate.}}{Na_2SO_4}.$$

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* *Jl. Soc. Chem Indus.*, 1895, p. 346,

The carbon dioxide evolved exerts pressure and forces the liquid, consisting of a solution of sulphate of soda and excess of bicarbonate highly charged with carbon dioxide, out of the "extincteur." The liquid escapes with rapidity from a narrow orifice, and can be directed in any desired direction, either by tilting up the whole vessel or, in the case of the larger sizes, by means of a short length of hose pipe.

The "extincteurs" usually contain 2 gallons of liquid, but others of 1, 5 and 7 gallons capacity are sometimes employed.

It is important in these extinguishers that an excess of bicarbonate of soda be employed, so that there can be no risk of damage from the oil of vitriol being brought into contact with articles of furniture, etc. If excess of bicarbonate be used the liquid is neutral or slightly alkaline, and cannot act corrosively upon any substance with which it may come in contact. A charge for a 2-gallon extinguisher, examined by the authors, was found to consist of about 11 ounces of sodium bicarbonate and 4 ounces of strong sulphuric acid, thus showing a decided excess of the former. Such a charge by its interaction would yield about 6 gallons of carbon dioxide, so that the pressure exerted by it would be 2 or 3 atmospheres; the liquid (2 gallons) would contain nearly 4 ounces of undecomposed sodium bicarbonate; this, together with the sodium sulphate, would perform the function of the salts used in hand grenades, viz., encrust the burning materials with an impervious layer and so obstruct the access of oxygen to it.

Many varieties of extinguishers are on the market, the chief differences among them being in the fittings, etc., and the methods of bringing the acid and bicarbonate into contact with each other. The plan most generally adopted is the one already described. In some American patterns sulphuric acid is replaced by oxalic or tartaric acid, both of which are solid and free from corrosive action.

The "Chemical Fire Engines" largely used in America, and recently coming into use in England, work upon much the same plan. One form consists of two steel or copper cylinders, each holding about 40 gallons of water.

The charge consists of 14 pounds of sodium bicarbonate and 7 pounds of sulphuric acid, the latter contained in a leaden jar. When the acid is admitted to the bicarbonate solution a pressure of 8 or 10 atmospheres is developed, by which a jet of liquid, highly charged with carbon dioxide, can be thrown 60 or 70 feet. The two cylinders work alternately, so that one can be recharged whilst the other is in operation, thus keeping up a continuous jet.

According to some authorities, the chief value of carbon dioxide in "extincteurs" and chemical fire engines is its action as a propelling agent; any advantage which the liquid expelled may possess over ordinary water is to be attributed to the salts dissolved in it, rather than to the carbon dioxide which it contains.

Other plans of applying carbon dioxide or other inert gases have been used. The waste gases from furnaces consist mainly of carbon dioxide, nitrogen and steam, and are practically free from oxygen. In some works arrangements are made so that these gases from the boiler flues can be conveyed, if required, into any desired room. The results are very satisfactory, any fire being quietly but promptly extinguished.

Another method of effecting much the same result is by the use of "extinguishing powders." These are of various composition, but always contain saltpetre (about

60%) with one or more oxidisable ingredients, *e.g.*, sulphur, charcoal, resin, etc., the sulphur being present usually to the extent of 30 or 40%. The ingredients are mixed in coarse powder, and sometimes, in order to render the combustion slower, a non-combustible material, such as sand or plaster of Paris, is added. They are often moulded into cartridges and provided with a fuse.

They burn with a bright flame, without explosion, and produce a large amount of smoke. Each pound yields about 5 cubic feet of gas, consisting largely of sulphur dioxide and carbon dioxide, and suffices to render about 200 cubic feet of space fire extinctive. Obviously, they can only be used in confined situations, and are very suitable for rooms in which inflammable vapours are liable to be evolved from drying operations, etc., where they are hung or placed in such positions that they are ignited at once in case of a fire, a condition, by the way, with which it is difficult to comply.

Ammonia gas (NH_3) has also proved of service for extinctive purposes. It is most conveniently applied in the form of *liquor ammoniac,* which is simply a strong solution of the gas in water, generally containing about 900 volumes of ammonia gas in 1 volume of the liquid. (See page 251.)

APPENDIX.

Table showing the boiling, flash, fire and ignition temperatures of some of the more commonly occurring substances.

A.—Solids.

Phosphorus	Boiling point,	280°C. (538°F)	Ignition point	60°C. (140°F)
Sulphur	" "	440°C. (837°F)	" "	250°C. (480°F)
Charcoal	" "	– –	" "	340°-800°C (640-1400°F (v. p. 67)

B.—Liquids.

Substance	*Boiling point*	*Flash point*	*Fire point*
Alcohol, absolute	78°C or 172°F	12°C or 54°F	
Alcohol with 0.5% ether		9°C or 48°F	
Alcohol with 2.5% ether		2.5°C or 36.5°F	
Ether	35°C or 95°F	below 0°C or 32°F	
Acetone	56°C (133°F)	" " "	
Carbon disulphide	46°C (83°F)	" " "	(ignites at 149°C)
Wood spirit	55-60°C (131-140°F)	ordin. temp.	
Turpentine	118°-185°C (248-364°F)	36-38°C (97-102°F)	
Rosin spirit	118-240°C (248-464°F)	36-38°C (97-102°F)	
Rosin oil	above 300°C (572°F)	130°C (266°F)	
Shale naphtha	82°-192°C (170-374°F)	ordinary temp.	
Benzene (benzol)	80°C (176°F)	−8°C (18°F)	
Benzine (benzoline)	50-60°C (122-140°F)	under −38°C (−36°F)	
Benzine (benzoline)	60-78°C (140-172°F)	−38°C (−36°F)	-30°C (-29°F)
Benzine (benzoline)	70-88°C (160-191°F)	−45°C (−49°F)	-42°C (-44°F)
Benzine (benzoline)	88-100°C (191-212°F)	−22°C (−8°F)	
Benzine (benzoline)	80-115°C (176-240°F	−22°C (−8°F)	-19°C (-2°F)
Ligroin	70-200°C (160-392°F)	under 0°C (32°F)	
Burning oil	120°-300°C (248-573°F)	21-45°C (70-113°F)	
Safety oil	150-300°C (302-572°F)	45-130°C (113°-266°F)	
Cleaning oil	200-300°C (392-572°F)	38-155°C (100-303°F)	
MINERAL LUBRICATING OILS			
Spindle oils	above 300°C (572°F)	160-190°C (320-374°F)	50-140°C higher
Machine oils	" " "	160-200°C (320-392°F)	
Cylinder oils	" " "	240-310°C (464-590°F)	
Tar Spirits	266-356°C (501-672°F)	38°C (100°F)	
Fatty Oils	decompose	200-260°C (392-500°F)	

C.—Gases. (See page 104.)

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